THE CHEMICAL EFFECTS OF ALPHA PARTICLES AND ELECTRONS

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BY

SAMUEL C. LIND, Ph.D.

PHYSICAL CHEMIST, U. S. BUREAU OF MINES

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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and

especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coordinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coordinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a

serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped therefore that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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AUTHOR'S PREFACE

In the decade preceding the recent European war, the subject of photochemistry first began to receive attention commensurate with its great importance. The experimental and theoretical aspects of the subject were presented in the well-known works of Plotnikow, Weigert, Sheppard, Benrath, and others.

The chemical effects produced by some of the other forms of radiant energy or matter have also been investigated, more or less fully, but the experimental results in this field have not hitherto been brought together in monographic form. The chemical effects of the various kinds of corpuscular radiation may be regarded as constituting one division of the general subject of *radiochemistry* (as defined in this monograph), of which photochemistry proper forms another division. The various effects, such as those of α and β particles, high velocity electrons, positive rays, recoil atoms, etc., have been regarded as being so indirectly related either to photochemistry or to radioactivity, that they have received rather scant treatment in the standard treatises on those two subjects.

It is the object of this monograph to collect the experimental material and, as far as possible, to present it in such a way as to emphasize the relations between the chemical effects of the *material* and of the *photochemical* radiations. The theoretical development has also been carried as far as the available data permit at the present time. In the main, however, the subject is still in the empirical stage and must await further evidence as to the behavior of individual atoms and gaseous ions before final conclusions can be drawn regarding the exact mechanisms of the radiochemical reactions.

The field of photochemistry has been touched upon, in the present work, only in comparing the nature of the various radiochemical effects, and also in connection with the Einstein photochemical equivalence law, which shows a close analogy with the ionic-chemical equivalence of the corpuscular radiant effects.

A fairly full consideration of the experimental tests of the photochemical equivalence law appeared to have additional justification, from the fact that the recent evidence has not yet been treated in the standard texts of photochemistry.

The subject of radioactivity has been introduced only in so far as was necessary to afford an insight into the principles and technique involved in the utilization of radioactive substances as sources of radiation in the production of the chemical effects under consideration. For the radioactive data included in this monograph, the writer is indebted to the following texts: Rutherford's "Radioactive Substances and Their Radiations" (1913), Mme. Curie's "Traité de Radioactivité" (1910), Meyer and v. Schweidler's "Radioaktivität" (1916), Bragg's "Studies in Radioactivity" (1912), and to J. J. Thomson's "Rays of Positive Electricity" (1913).

The writer is also greatly indebted to the cooperation of the Editors of the Scientific Monographs of the American Chemical Society, who have supervised the publication of the present monograph, to Dr. G. L. Wendt of the University of Chicago for his very helpful suggestions and criticisms, and to the Chemical Catalog Company, Inc., which has efficiently carried out the plans of the Editors.

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COIMBATORE

THE CHEMICAL EFFECTS OF ALPHA PARTICLES AND ELECTRONS

Chapter 1.

Radiochemistry.

1. Definition of Radiochemistry.

The relationships existing between the various forms of energy and the transformations of the different kinds into one another are of fundamental importance in the physical sciences. The chemist is primarily concerned with those transformations in which chemical energy is one of the forms involved. Thermo- and electro-chemistry represent two of the most highly developed branches of physical chemistry and deal with the relations between chemical energy on the one hand and thermal and electrical energies, respectively, on the other. Of no less importance are the relations between chemical and *radiant* energies, which constitute a subject that should, according to the same system of terminology, be designated as *radiochemistry.*

The term radiochemistry has already been used otherwise by some authors to designate the chemistry of the radioactive elements and of their transformations by atomic disintegration. Since this more special usage is relatively new and not thoroughly intrenched, and since the term radiochemistry is the only logical one to conform with such terms as electro-, thermo-, photochemistry and radiotherapy, it appears desirable to adopt the use of the term radiochemistry in the broader sense, exactly analogous to and including that of photochemistry, in the sense that all relations between chemical energy and any form of radiant energy or matter should be comprehended by the term *radiochemistry.*

2. Radiant Energy and Matter.

In the strictest sense, perhaps, radiochemistry should deal only with truly radiated energy to the exclusion of the kinetic energy of projected particles of matter such as α particles or of electrons and β particles. This would practically narrow the subject to that of photochemistry itself. It is not only a matter of convenience to include also the relations involving material particles, but the relationships and reactions are in many ways so similar, and the analogies of such far-reaching importance, that it forms one of the chief objects of the present work to treat both from the same standpoint, without any particular distinction as to the vehicle of the *radiated* energy.

The forms of radiant energy or matter to which attention will be given are: α and β particles, γ rays, recoil atoms, positive rays, electrons including the various forms of electrical discharge such as corona, silent and spark discharges, and, to a certain extent, visible and ultraviolet light and X rays. The differentiation in terms involved in the usage α or β *particle* and γ *ray* will not be adhered to strictly. For the sake of brevity, free use will be made of the older terms α and β *rays*.

3. Photo- and Radio-Chemistry.

A full appreciation of the vastly important function of light in our terrestrial economy, both past and present, in transforming and storing chemical energy will serve to emphasize the importance of photochemistry. While it can not be claimed that either the recognition of the relative position of photochemistry or the actual beginning of the science is new, it is only within the decade preceding the recent European war that its development may be regarded as commensurate with its preeminent importance. Compared with the state of development in thermo- or electro-chemistry, photochemistry must be conceded to be in its beginning and not yet past the first stages of empiricism.

It appears unnecessary to seek far afield, as some authors have done, for the causes of the slow development of photochemistry. The earlier development of one of its technical branches, *photography,* doubtless contributed to the neglect of the mother science, as has been suggested by Luther,[1] but other con-

[1] R. Luther, Bunsengesellsch. 1908; *Zeit. f. Elektrochem.*, *14*, 445-53.

tributing factors demand consideration, such as the difficulties presented by the intricate technique of photochemical experimentation, the necessity of awaiting progress in the sciences of radiology and of atomic structure, and also the early unfortunate overemphasis of the *catalytic* nature of photochemical phenomena.

As has been stated in the preface several treatises have appeared which deal very adequately with the subject of photochemistry. It is not the purpose of the present monograph to duplicate this field, but rather to attempt to extend it by presenting the experimental results of the investigation of chemical reactions brought about by some other forms of radiant energy, such as electrical and radioactive discharges, with the object of pointing out those analogies and differences which appear to exist.

The general subject of radiochemistry is, like photochemistry, still in the experimental stage and must be approached from the empirical side without any expectation of arriving at once at final principles. It is therefore the object of this work to present the experimental results for the chemical effects of some of the other forms of radiant energy than light in the hope that their examination and comparison with the results of photochemical investigations may contribute to a somewhat more comprehensive view of the field of radiochemistry as a whole. Although the branch of radiochemistry to be treated is of recent development and has been open, on account of the scarcity of some of the necessary radioactive material, only to a limited number of investigators, nevertheless, very definite results have been obtained for a few reactions and some principles have been established that appear to have fairly general applicability.

Chapter 2.

Brief Outline of Radioactivity and Some Properties of the Radiations.

4. Nature of Radioactivity—Rutherford-Soddy Hypothesis.

While it lies outside the province of radiochemistry to consider the subject of radioactivity in its entirety, it is impossible to treat the chemical effects of the radiations accompanying and produced by radioactive changes without giving some attention to the various radioactive elements and their radiations.

Historically it is interesting to recall that the discoveries both of X rays by Roentgen and of radioactive radiations by Becquerel were made through the means of their radiochemical actions on the photographic plate. Although other more convenient methods of investigation were soon developed, the photographic method has continued to play a rôle of some importance.

The continuous emission of heat and of radiations was one of the first properties of radioactive substances to be observed, and also proved to be one of the most puzzling since it appeared to contravert the law of the conservation of energy. In looking for a general theory of radioactivity it appeared to Pierre Curie and A. Laborde[1] not impossible that radioactive matter might be merely the receptor of a form of radiant energy coming from extraterrestrial sources and capable of affecting only the elements of heaviest atomic weight. To ascertain if the sun might be the source of the supposed radiant energy, comparison was made of the activity of a radioactive substance measured at noon and again at midnight to find if the interposition of the earth's thickness would diminish the activity. A negative result was obtained.

Although it was early suggested that radioactivity is purely an atomic phenomenon, it was not until 1903 that Rutherford

[1] P. Curie and A. Laborde, Comp. rend., 136, 673 (1903).

and Soddy[2] proposed and elaborated a concrete theory of successive atomic disintegration which explained all the phenomena exhibited by radioactive substances, and left no doubt that the source of radioactive energy and radiation is from within the radioactive atom itself. All subsequent investigations have only strengthened this hypothesis, until now it is supported by a chain of evidence, both experimental and theoretical, which is unique in its completeness and perhaps without parallel in the physical sciences.

5. Radioactive Phenomena.

Radioactive substances exhibit the following striking properties:

(1) The continuous emission of heat.
(2) The continuous emission of certain rays and particles.
(3) The production of luminescent effects in some substances.
(4) The ionization of the surrounding air (or of other gases).
(5) The production of chemical reaction in substances subjected to radiation.
(6) The production in some substances of certain effects such as color, thermoluminescence, etc., which may or may not be due to chemical action.

The most notable of these phenomena is the emission of electrically charged particles at high velocity from the radioactive atom, due to some internal disturbance of the electrical equilibrium of the atom, the cause and exact nature of which are not yet wholly understood. All of the other phenomena enumerated may be regarded as secondary effects of the radiations.

6. Kinds of Radiation.

Three distinct kinds of radiation are emitted by the various radioactive substances: α particles, β particles, and γ rays.

α *Particles.* The corpuscular nature of α particles was first

[2] Rutherford and Soddy, *Phil. Mag.* (6) 4, 370; 569 (1902), 5, 441; 576 (1903).

suggested by Mme. Curie[3] in 1900 to explain the peculiarities of their absorption or loss of energy in passing through matter. Strutt[4] suggested their being positively charged, Rutherford[5] demonstrated their deflection both by magnetic and by electrical fields. Later Rutherford and his co-workers[6] showed that α particles are doubly positively charged helium atoms. They are emitted from the radioactive atom at a very high initial velocity (1/15 to 1/20 that of light), and since they possess mass of atomic dimensions, they represent an enormous concentration of kinetic energy. In fact the α particle is the most powerful agent yet known to science and in all probability will remain so, as it is hardly conceivable that any means will ever be devised of imparting to ponderable matter a velocity exceeding that at which the α particle is dispelled from the atomic nucleus. It is therefore not surprising that we find in the α particle a powerful agent in bringing about ordinary chemical changes in matter with which it comes into contact, but, as Rutherford[7] has recently shown, at least two kinds of atoms (nitrogen and oxygen) when squarely struck by an α particle are completely altered, producing hydrogen or helium atoms (see Chapter XII). Of the total energy emitted by radioactive substances, by far the larger proportion is carried by the α particles, and it is principally the transformation of this energy that results in the production of the thermal, electrical and chemical effects already referred to.

β *Particles.* The β particles emitted by radioactive matter have been proved by numerous authorities to consist of electrons, singly charged atoms of negative electricity, ejected from the nucleus of the radioactive atom at varying velocities, in some cases approaching closely to that of light.

γ *Rays* for a long time presented an unsolved problem as to their exact nature and origin. They are emitted only by substances which also emit β particles and evidently are connected with this emission. It is now generally conceded that they consist of ether pulses of very short wave length and therefore have the general properties of light and may be most aptly compared

[3] Mme. Curie, Comp. rend., 130, 76 (1900).

[4] R. J. Strutt, *Phil. Trans. Roy. Soc.* A 196, 507 (1901).

[5] E. E. Rutherford, *Phil. Mag.* (6) 5, 177 (1903); *Phys. Zeit.*, 4, 235 (1903).

[6] Rutherford and Geiger, *Proc. Roy. Soc.* A 81, 162 (1908). *Phys. Zeit.*, 10, 42 (1909). Rutherford and Royds, *Phil. Mag.*, 17, 281 (1909).

[7] Rutherford, *Phil. Mag.* (6) 37, 537-587 (1919).

with X rays, except that they greatly exceed in shortness of wave length and penetrating power any X rays that have yet been produced. A fuller discussion of the properties of these three kinds of radiation will be found in subsequent paragraphs.

Recoil atoms also constitute a form of radiation that has been shown to produce chemical effects. A recoil atom is the remainder of a radioactive atom just after the emission of an α (or β) particle while it is still in rapid motion owing to the "recoil" action. Ionization and other radiation effects are produced. Further reference to recoil atoms will be found in Chapter XI.

7. Radioactive Families and Their Transformation Products.

Of the common elements only two, uranium and thorium, have been found to possess distinct radioactive properties. Each of these two elements is the parent of a series of radioactive elements undergoing atomic decay. There is also a third family having as its parent, actinium, an element of very rare occurrence, apparently a side-chain offspring of the uranium series. These three families comprise about thirty-five members which differ from each other in chemical, physical and radioactive properties, the latter being characterized by the radiations emitted and by the rate of change of one element into the next lower member in the series. Employing the usual terminology of chemical kinetics, each simple radioactive change has proved to be *mono-molecular,* and not only corresponds perfectly to the requirements of the logarithmic equation of the so-called *first order* reactions, with respect to time rate of change, but the rate of change persists unaltered no matter to what physical or chemical influences it may be subjected. A simple radioactive transformation represents *par excellence* the first order reaction. The rate of change is usually formulated as: $E=E_0.e^{-\lambda t}$, in which E_0 is the initial quantity of radioactive material undergoing change, and E the quantity remaining unchanged after the lapse of any interval of time t, e is the base of the Naperian logarithmic system, and λ is the decay constant, by which is meant the fraction of the total which changes in unit of time; λ is the reciprocal of θ, the *"average life"* of a radioactive element, which is not to be confused with the term "half period" of the element. The *half period* is the time in which just one-half of the initial quan-

tity undergoes change; and, as is also the case for all first order reactions, it makes no difference what time or quantity is chosen as initial. The relation between the two is: average life (θ) = half period x nat. log *2* (= 1.4428). It may be mentioned that the usual f[illegible] of the differential equation for first order reaction[illegible] -x)[8] can be readily converted into the form given above for radioactive changes. The average life for a given element is its most fundamental physical constant, and is found to vary for the different elements from a very small fraction of a second up to several billion years. As far as known the reactions are irreversible.

Uranium and thorium are the two elements possessing the highest known atomic weights, and the property of radioactivity does not seem to be possessed by elements of atomic weight less than 210, excepting, perhaps, potassium and rubidium, which have been shown[9] to emit β rays.

According to the Rutherford and Soddy hypothesis one atom of a radioactive substance A changes to form one atom of substance B, and in case of the emission of α particles, one atom of helium is ejected from each atom of A in changing to B. It follows that B must have an atomic weight four units lower than that of A, also that the enumeration of the α particles emitted serves as a measure of the rate and quantity of change, and also that the accumulation of helium gas over a known period may serve as a measure of the same constants; or, *vice versa*, if the rate of change be known, the accumulation of helium is a measure of the period of time during which the accumulation has taken place. Reference to the fuller texts on radioactivity[10] will show that all these factors have been abundantly verified experimentally and fit into the network of evidence confirming the Rutherford and Soddy theory of radioactive change.

8. Radioactive Equilibrium.

Although the radioactive changes, as already stated, are irreversible and hence incapable of attaining a state of equilibrium

(8) S. L. Bigelow, "Theoretical and Physical Chemistry," p. 353 (1912). K. G. Falk, "Chemistry of Enzyme Actions," p. 22 (1921).

9 N. R. Campbell and A. Wood, *Proc. Camb. Phil. Soc.*, 14, 15 (1907).

10 Rutherford, "Radioactive Substances and Their Radiations" (1913). Mme. Curie, "Traité de Radioactivité" (1910). Meyer and von Schweidler, "Radioaktivität" (1916).

in the ordinary way of reversible reactions, yet a state of dynamic equilibrium may be attained between a parent element and one or more of its decomposition products. This occurs through the change of the product, not back into the original, but into new products at the same rate that it is being produced from the parent. Thus the parent element, which is producing its decay product at the same rate that the latter is undergoing further change, has attained a state of dynamic equilibrium in which a constant ratio between the quantities of the two elements involved is maintained. Such radioactive equilibrium may apply to a whole family or to any part of a family, beginning with a parent element of longer life than its products. For example, uranium in nature, after the lapse of geological ages, is found to be in equilibrium with all the members in its family. Radium attains equilibrium with its next succeeding decay products in about one month, while radium emanation reaches equilibrium with its immediate products in four hours.

From the physical-chemical standpoint these equilibria represent nothing different from what one should expect from a series of successive irreversible mono-molecular reactions. By the superposition of equations of the first order Rutherford[11] has dealt with the equilibria, which on the whole must be regarded as the most complete series of successive reactions known to physical chemistry. They may appear intricate on account of their number, but otherwise they are wonderfully simple and free from complications such as would arise in the treatment of ordinary chemical reactions.

From the radioactive standpoint the dynamic equilibria are of great importance from the following considerations: When two or more radioactive elements are in equilibrium, the number of atoms of each element being formed and decaying per unit of time is the same. Throughout a whole system of elements in radioactive equilibrium, the number of atoms of each element changing per unit time is identical and is also measured by the number of α particles being emitted per unit of time by any member of the system. This means of course that equilibrium quantities of all elements in the same radioactive family emit the same number of α particles per second. For example, if one gram of radium emits 3.72×10^{10} α particles per second, that

[11] Rutherford, "Radioactive Substances and Their Radiations," Chapter 11.

quantity of any other member of the uranium family which would be in equilibrium with one gram of radium would also emit the same number of α particles per second. This makes it evident that in choosing units for radioactive elements it is much simpler to deal with the equilibrium quantities rather than with absolute masses, particularly since many of the radio-elements can not be obtained in ponderable quantities and are measured only through some radiant property. Such a system of units was devised and adopted at the direction of the International Congress of Radiology and Electricity, Brussels, 1910. One gram of elemental radium was chosen as the basic unit. Standard preparations of radium were prepared by Mme. Curie in Paris and by Hönigschmid in Vienna from which secondary standards[12] have been furnished to all the principal countries for the standardization of radium by means of its γ radiation. That quantity of any other member of the uranium family in equilibrium with one gram of radium has been called the *curie*, a unit which has come into universal use for radium emanation, and which has been subdivided into milli- and micro-curies, signifying the thousandth and millionth parts, respectively.

9. Kinetic Energy of α Particles.

Since all α particles are doubly charged helium atoms it is evident that those from the different radioactive substances can differ from each other only in the initial velocity with which they are emitted; and that furthermore, when one α particle has lost velocity until it has just become equal in velocity to one emitted at a lower value, from that point on the two will have identical properties in the same medium. These statements have been fully proved by W. H. Bragg,[13] who has also shown that all the α particles emitted by the same kind of radioactive substance have the same initial velocity, which means that they are possessed of the same kinetic energy and in the same medium will have the same penetrating power and other properties identical.

[12] Meyer and v. Schweidler, "Radioaktivität" (1916), p. 210.

[13] W. H. Bragg, "Studies in Radioactivity" (1912); Bragg and Kleeman, *Phil. Mag.* (6) 10, 318-40; 11, 466-84; W. H. Bragg, *ibid.*, 11, 617-32; 13, 507-16; 14, 425.

10. Range of α Particles.

The distance which an α particle can penetrate in a given medium before its kinetic energy is dissipated is called its *range.* The range usually refers to a gaseous medium, but the same term is used for penetration in liquids or solids. It is believed that at the end of its range, as observed by the cessation of gaseous ionization, the kinetic energy of an α particle is reduced practically to zero, though there has been some question on this point. It has been shown by Duane[14] that the α particle loses its ability to produce ionization, luminescence and chemical action simultaneously. Either ionization or luminescence may be used to determine the range, preferably the former.

The following Table I shows the members of the uranium-radium family in the order of their sequence, indicates the kind of radiation accompanying each transformation and its half period; and for α particles shows the range in air at 15° and 760 *mms., the initial velocity, and the total number of pairs of ions* produced by a single α particle in its whole range.

11. Ionizing Power of α Particles.

An α particle projected from an atom with enormous velocity travels in a straight line penetrating all the atoms encountered in its path. By penetration is meant that the α particle passes through the electrical field due to the electrons surrounding the atomic nucleus of positive charge, as conceived in the Rutherford-Bohr[15] atomic model. According to Rutherford's idea, resulting from the study of the deflections of α particles near the end of their paths, an atom consists of a very small positive nucleus with an elemental charge a little less than one-half the atomic weight, surrounded by electrons equal in number to the positive nuclear charge, situated in rings at relatively great distance from the positive nucleus. According to this idea of atomic structure which has now become generally accepted, it is evident that an α particle may pass through a large number of atoms without ever coming close enough to the nucleus to have its course altered, as long as its velocity is great.

[14] Wm. Duane, Comp. rend., *146,* 958-60 (1908).

[15] Rutherford, *Nature,* 92, 423 (1914) ; *Phil. Mag.* (6) 27, 488-98 (1914). N. Bohr, *Phil. Mag.* (6) 26, 1-25; 476-502; 857-75 (1913).

TABLE I

Uranium-Radium Disintegration Series

Series Member	Atomic Weight	Half Period	Rays	α Particles		
				Range cms. air at 15° C.	Init. Veloc. 10^9 cms. sec.$^{-1}$	Total pairs of ions in air x10^5
U_I	238	4.5x10^9 yrs.	α	2.50	1.37	1.20
UX_I	234	23.5 days	β	....	....	....
UX_{II}	234	1.1 min.	β, γ	....	....	....
U_{II}	234	2x10^6 yrs.	α	2.90	1.44	1.33
Io	230	10^5 yrs.	α	3.07	1.46	1.38
Ra	226	1580 yrs.	α	3.52	1.53	1.45
Ra Em	222	3.85 days	α	4.16	1.62	1.69
Ra A	218	3.05 min.	α	4.75	1.69	1.84
Ra B	214	26.8 min.	β, γ	....	....	....
Ra C_1	214	19.6 min.	α	6.94	1.92	2.37
Ra C′	214	10^{-6} sec.	β, γ	....	....	....
Ra D	210	16 yrs.	β, γ	....	....	....
Ra E	210	4.85 days	β, γ	....	....	....
Ra F	210	136 days	α	3.83	1.58	1.60
Ra G (Pb)	206	∞	Rayless	....	....	....

As may be seen in Table I, a single α particle from Ra C produces in its entire path in air 237,000 pairs of ions, which means that it detaches this many electrons from the atoms encountered. Using his classical oil droplet method, Millikan[16] has recently shown for several of the common gases, including air, that only one electron is detached by an α particle from each molecule, leaving a singly positively charged residual molecule or ion. This process of ionizing requires a certain expenditure of energy which continues to lower the kinetic energy of the α particle by reducing its velocity until it is no longer able to produce ionization, which marks the end of its range. Unless acted on by an external electrical field the positive and negative ions thus separated would recombine and the net result of the expenditure of energy would be the production of heat (assuming that no permanent chemical action has resulted); or inversely, the heat evolution of radioactive substances emitting α particles is a measure of the total energy available for ionization. From a knowledge of the total number of ions, the energy necessary to produce one pair of ions in air has been calculated to be 5.5×10^{-11} ergs.[17]

The property of producing ionization not only constitutes the most delicate test for radioactive substances but also forms the basis of their quantitative measurement. Furthermore, as will be shown in Chapter VII, the relation between the ionization and the chemical effects of the radiation is in many cases of importance. In radiochemistry one is interested not only in the total ionization produced by an α particle but also in the distribution of the ionization along the path of the particle. This subject has been carefully investigated by Bragg, Geiger and others.[18] Fig. 1 represents the ionization curve for a single α particle from Ra C in air, in which the length of path is plotted as abscissæ and the number of ions (pairs) as ordinates.

The form of the curve shows that for the first two or three centimeters of path the ionization remains practically constant at about 2.2×10^4 pairs of ions per cm. of path traversed. The number then begins to rise and increases quite rapidly toward

[16] R. A. Millikan, V. H. Gottschalk, M. J. Kelly, *Phys. Rev.* (2) 15, 157-77 (1920).

[17] Rutherford, "Radioactive Substances and Their Radiations," p. 159.

[18] W. H. Bragg, "Studies in Radioactivity," Chapters 3 and 4. H. Geiger, *Proc. Roy. Soc.*, 82, 489 (1909).

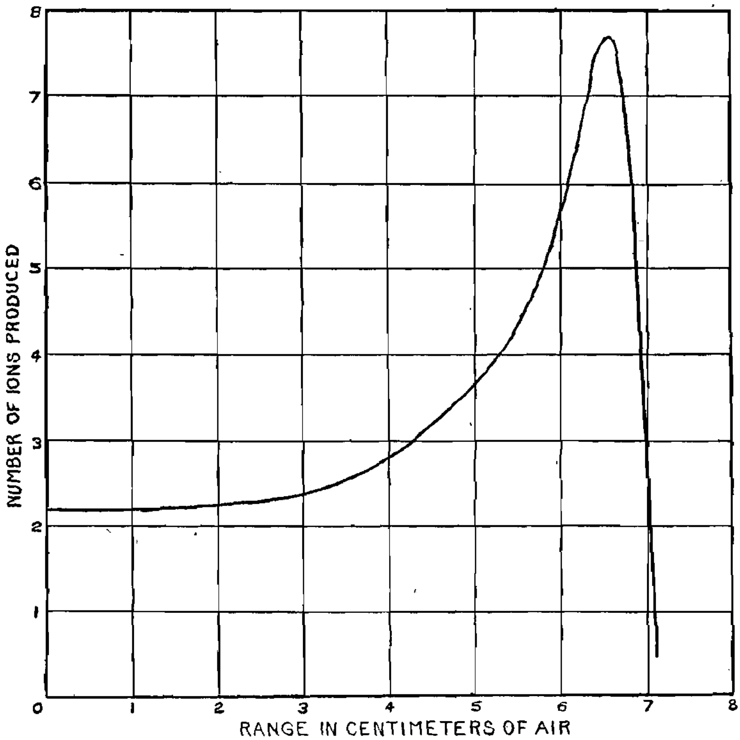

Fig. 1.

the end of the range and then drops almost abruptly to zero. The total number of ions produced in the whole course is evidently represented by the area within the curve. Since α particles from any other source are identical except in initial velocity, their ionization curves would be identical after any point at which they attain the same velocity as that represented on the curve for Ra C. For example, the curve for Ra A would be represented by counting backward from the end of the curve *4.75 cms.*, the length of the range of the α rays from Ra A. Similarly if either end of the path of an α particle is incomplete through the interposition of a partial screen, or if the ray is absorbed in another medium before completing its course, the effective ionization may still be obtained by referring only to the effective part of the path.

It has been shown by Geiger[19] that the ionization curve for an α particle corresponds to a relation between the velocity (v) and the range (R) of the form: $v^3 = \text{const.}xR$, and that the ionization, $(I) = \text{const.}xR^{2/3}$, from which it follows that the total ionization of a single α particle $(k) = k_0R^{2/3}$, in which k_0 is a constant with the value $6.76x10^4$.

12. Enumeration of α Particles.

From what has been said in the foregoing paragraphs it is evident that the counting of the number of α particles emitted per unit time by any given radioactive substance is very important. Since the number being emitted from an active substance like radium is very large ($3.72x10^{10}$ per gram per second), it is necessary to reduce both the quantity of substance and the solid angle from which the effective radiation is received. Two methods of detecting and counting the particles have been employed: (1) by observation of the number of scintillations produced on a phosphorescent ZnS screen under low magnification, each spark corresponding to the impact of one particle; (2) by observation of the number of deflections of an electrometer in series with a condenser in which the α particles are received. These two entirely different methods have given concordant results for the value for radium.[20] From the statements in § 8 it is clear that any other member of the uranium-radium series which emits α particles will emit this same number per second from the equilibrium quantity. For example, the emission from radium in equilibrium with emanation, Ra A and Ra C will be four times the number per gram of radium; the emission from one curie of emanation in equilibrium with Ra A and Ra C would be three times this same number. While the number, thirty-seven billion helium atoms, ejected per second from one gram of radium, appears very high, it should be remembered that at even this rate of decay, the half period of radium is 1580 years, accounted for by the tremendous number of atoms represented in one gram or even one cubic centimeter of a gas, which is of the order of billions of billions.

[19] H. Geiger, *Proc. Roy. Soc.*, 83A, 505 (1910).
[20] Rutherford, *Phil. Mag.* (6) 28, 320-7 (1914).

13. Some Additional Properties of α Particles.

The great kinetic energy possessed by an α particle compared with that of even the swiftest β particle (roughly 100 times as great) is due to the large mass of the former, approximately 7,000 times that of an electron. The α particle collides with a large number of molecules in a short path, thus limiting its total penetrating power in spite of its great momentum. Hence α particles must be classed as non-penetrating radiation. As may be seen in Table I, they have ranges in air at ordinary pressure of 3 to 8 cms., and penetrate other substances in the inverse order of the "stopping power" of the given substance.

Stopping Power. The term stopping power of a substance, referring to its power to stop α particles, was first introduced by Bragg.[21] Proceeding from the generalization that the α ionization curves of different gases differ from each other only in a shortening or lengthening of all the ordinates or abscissæ by the same ratio, the following very simple procedure was proposed by Bragg. Instead of having to determine the complete curve of ionization for each gas it is only necessary to find the ionization, *I,* at one particular point, *R,* in the path of an α particle. If I′ and R′ are the corresponding values for air, the ratio of the total ionization (k) in the two media may then be expressed by $RI/R'I'=k/k'$ (1); and putting k′, the total ionization for air equal to 1, the total ionization of any gas is referred to that in air and may be called the *total specific ionization.* But if it is desired to refer not to the total ionization, but to that produced along a certain length of path, which is evidently equivalent to referring to the relative ionization in a single molecule of each gas, or in any equal number of molecules of each gas, one must use the ratio I/I', which can be shown to be equal to Bragg's *ks,* in which *s* is the stopping power, as follows: Putting the reciprocals of the ranges R and R′ equal to s and s′, the respective stopping powers, and substituting in equation (1) above: $I/I'=ks/k's'=ks$, by putting k′s′ for air equal to 1. This value may be called the molecular specific ionization (Bragg's ks) to distinguish it from the total specific ionization (k). In Table II will be found the values for a number of common gases and other substances taken from Bragg.[22]

[21] W. H. Bragg, "Studies in Radioactivity," Chapters 5 and 6 (1912).
[22] *Ibid.* p. 65 (1912).

TABLE II

Stopping Power and Ionization (by α Rays) of Different Gases According to Bragg

	k x 100	s x 100	ks x 100
Air	100	100	100
H_2	100	24	23.3
N_2	96	98.9	94
O_2	113	106.4	109
CO	101.5	98.5	100
NO	....	....	128
CO_2	103	150.5	152
N_2O	105 (99)	146	153
NH_3	90	....	81
CS_2	137	218	299
SO_2	103	....	201
He	....	20.1	21.1
Ar	....	95.1	124.5
Br	....	....	390
HBr	129	....	....
HI	129	....	....
HCl	129	....	....
CH_4	118	86	110
CH_4O	122	....	174
C_2H_2	126	112	140
C_2H_4	122	135	165
C_2H_6	130	151.4	197
C_5H_{12}	135	354.4	485
C_2H_6O	123	200	246
C_6H_6	129	333	430
CH_3I	133	258	343
C_2H_5I	128	312	400
$CHCl_3$	129	316	408
CCl_4	132	400	528
CH_3Br	132	203	275

Stopping Power (*s*); Total Ionization (*k*); and Molecular Ionization (*ks*).

Bragg's generalization in regard to stopping power does not hold strictly for different substances but approximates closely enough to be of service for all practical purposes in radiochemistry.

It will also be of general interest to note that the study of the stopping power of different substances for α particles is not

confined to gases. By the use of very thin sheets as screens the stopping power of the heaviest metals has been determined and may be translated into terms of air equivalent. Bragg and his co-workers have found (*loc. cit.*) that the stopping powers of the various metals are proportional to the square roots of their atomic weights. The same relationship holds approximately even for gases as light as air and hydrogen. Bragg has also found the stopping power to be an atomic property which is additive in the compounds of the elements. The same does not hold, however, for specific ionization, which is by no means additive for compounds. This must mean that the manner in which the atoms are held together has an influence on the ease with which electrons can be detached, and since it is now generally agreed that the atoms are held together by means of the electrons, this reasoning appears all the more plausible. From Table II it can be observed that as the molecular weight of chemical substances increases, the easier it becomes for α particles to produce ionization in them.

14. Characteristics of Members of the Radium Family as Sources of Radiation.

Up to the present only members of the radium series have been used quantitatively in studying radiochemical effects. The members preceding radium in the series are all so weakly active that they do not come into consideration as artificial means of investigating radiochemical effects, but in nature they play a rôle which will be given special attention in some of the later chapters of this work. This statement as to the effects in nature would apply equally well to the members of the other radioactive families.

Radium itself has no general applicability except in equilibrium with its products through Ra C, which necessitates its being maintained in a sealed container on account of the gaseous nature of radium emanation. Owing to the non-penetrating character of α rays, only β and γ radiation would be obtained through the walls of the container. Radium salts sealed in glass tubes, therefore, constitute the most convenient source of penetrating rays, having the advantage of constancy of radiation after the first month subsequent to sealing, but the disadvantage

that it is usually difficult to determine what part of the radiation is effective in a given absorbing system under working conditions. Radium in equilibrium with Ra C has four sets of α particles, one each for Ra, Ra Em, Ra A, and Ra C. (See also § 8.)

Radium Emanation represents one of the most convenient and most used sources of radiation. It can be handled as a gas, can be measured with ease, and can be introduced into the interior of many systems in very small volume. The volume of 1 curie of emanation (the quantity in equilibrium with 1 gm. of Radium) is only 0.58 $mm.^3$ and furnishes a very concentrated form of radiation. It does not, unlike radium salts, appreciably absorb its own radiations. On account of its relatively short life, it has no permanent value and can therefore be subjected to danger of loss, breakage, etc., in ways that would not be feasible with radium salts. Practically, its only disadvantage consists in its short life and continually changing activity, but since this change takes place according to a perfectly well established and invariable law, it can readily be taken into account. Its radiations include those of Ra A, Ra B, and Ra C, with which it attains equilibrium after four hours in a closed vessel.

Active Deposit. Ra A, Ra B, and Ra C together constitute the so-called *active deposit* of radium emanation formerly called also "induced activity," because they are deposited as solids on the walls of a containing vessel or on any surrounding objects to which the emanation may diffuse and owing to their activity appear to impart to these objects a temporary radioactivity. Ra A emits only α rays, Ra B only rather non-penetrating β and γ rays. On account of the extremely short life of Ra C′ (10^{-6} sec.), both Ra C_1 and Ra C′ will be, in the following pages, referred to collectively as Ra C, which then constitutes not only a source of α rays, but also of the most penetrating β and γ rays in the radium series. The γ rays of Ra C furnish the best means of measuring either radium or radium emanation.

Radium D and E possess no rays of radiochemical importance. Ra F (polonium) is unique in furnishing only α rays and is the most convenient source of this form of radiation free from penetrating rays. It is usually deposited electrolytically on copper, which then, of course, absorbs that half of the α radia-

tion directed toward it. Especially for use in liquid systems, polonium is a very suitable source of α rays.

As generally applicable to all α particles, it should be mentioned that Rutherford and Geiger[23] utilized the α radiation from polonium to determine the probability variations of the emissions of α rays both with respect to time and space and found their distribution fully obeying the laws of chance.

[23] Rutherford and Geiger, *Phil. Mag.* (6) 20, 698-704 (1910).

Chapter 3.

Electrical Effects—Ionization.

15. Saturation Current as a Measure of Ionization.

The general principle of the method of the measurement of gaseous ionization deserves at least brief consideration. Let us suppose that the air in a closed chamber provided with electrodes is subjected to a constant radiation that will produce a fixed number of ions in the chamber in unit time. Connect the electrode terminals, which must be carefully insulated from the chamber and from the surrounding air, in series with an instrument capable of measuring low electrical current, such as a quadrant electrometer. Apply from a high voltage battery successively increasing voltages and plot a current-voltage curve as in Fig. 2. For low voltages the curve rises linearly, indicating that the current increases in direct proportion to the applied voltage just as would be required by Ohm's law in a conductor of the first class. On applying yet higher voltage the current rises more slowly than the voltage and finally reaches a constant maximum in the part of the curve AB (Fig. 2) which remains horizontal. It can now be inferred that all the available ions are being drawn to the electrodes and are discharged, and that further increase of voltage within suitable limits produces no increase of current. This current is designated as *saturation current,* which is evidently a direct measure of the total number of ions being formed per unit time in the chamber. It is also inferred that under conditions in which insufficient voltage is applied the ions not attracted to the electrodes recombine with each other by ordinary diffusion.

The potential that must be applied to produce saturation current will depend on the strength of the ionization and the gaseous pressure, the lower the pressure the smaller the required voltage. At atmospheric pressure 2,000-5,000 volts per cm. will suffice in most cases. However, if the ionization is very great, such as that produced by a strong α ray source, it becomes impossible

to produce saturation current. The measurement even of moderate ionization produced by α rays has been found to present especial difficulties, supposedly due to the high concentration of ions along the path of the particle. One is seldom able to measure directly the ionization of α rays of an intensity suitable for

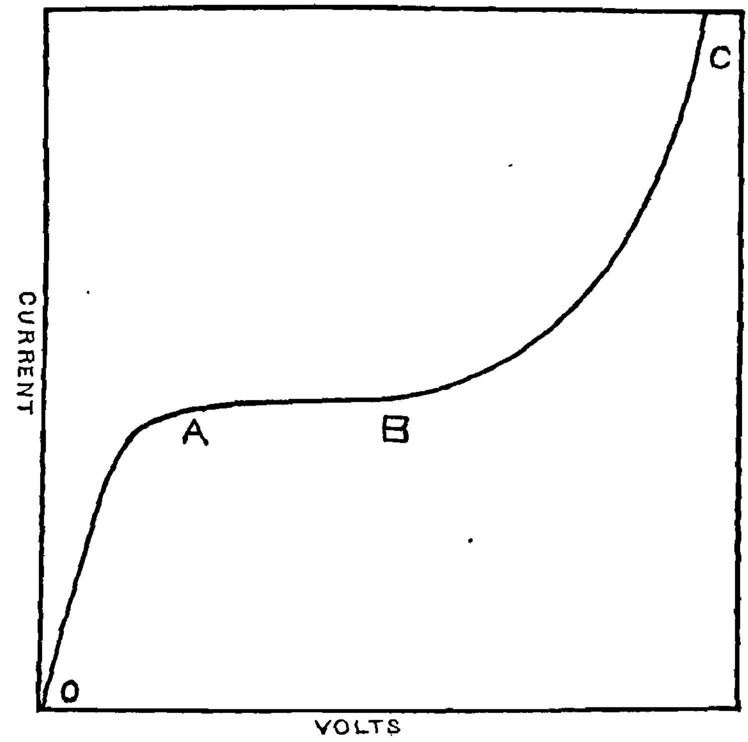

FIG. 2.

the measurement of its chemical action also, and must resort to indirect methods of calculating the ionization which will be treated in Chapter VII.[1]

[1] In connection with the measurement of gaseous ionization by means of saturation current, it should be pointed out that while the practice among physicists of referring to the total number of *pairs of ions* is fairly common, the expression *ions* where *pairs of ions* is meant is also unfortunately prevalent. This is particularly confusing to the chemist, who in dealing with electrolytic ions in connection with the solution theories, always means total positive and negative ions, never ions of only one sign. Naturally the physicist in taking current units as the measure of gaseous ionization is prone to neglect the other half of the ionization, thus leading to confusion in cases where the number of ions of both signs is important.

16. Ionization by Electronic Shock.

To return to the curve in Fig. 2, if the voltage be increased beyond that necessary for saturation current, the electrons and ions attain still greater velocities, and soon the electrons reach velocities within their free paths, at which their kinetic energy becomes sufficient to ionize the gas molecules with which they come in contact, thus increasing the total number of electrical carriers beyond the number being produced by primary radiation. Owing to the rapid increase in the number of carriers the current again begins to rise, as indicated by the curve BC, on account of this process which has been called ionization by "shock" or collision.

As will be later shown (§ 52) this form of ionization probably plays a very important part in the chemical action produced by electrical discharge through gases. Evidently there is no limit to the current resulting from such an increase in voltage until the sparking potential is reached. The current resulting from ionization by shock usually will not represent a condition of saturation. At ordinary gas pressures, only a small fraction of the total number of ions produced by an intense discharge reaches the electrodes before recombining, and it is only this small fraction, of course, which carries the current; the other ions may recombine to form the original product, or may combine to form a new chemical product, hence their interest in radiochemistry.

X ray Tubes may be very aptly employed to illustrate ionization by shock. The old ordinary form of X ray tube depends upon shock ionization for a sufficient number of carriers to conduct the current, which explains why the gas pressure had to be held within rather narrow limits; if too high, the free path of the electrons was too short to enable them to obtain the necessary velocity to produce ionization by shock; if too low, not enough encounters resulted to maintain discharge. The ordinary X ray tube has a well known tendency to become "hard" by reduction of the gas pressure, which is also a result of ionization. It means that some of the positive gas ions attain a velocity sufficient to cause them to adhere to the electrode upon reaching it, thus reducing the pressure. Whether the effect is chemical or physical has not been definitely determined. The

same general type of "clean up" may be illustrated by passing a discharge through radium emanation in a small Geissler tube. After the tube has operated for some time under suitable conditions, it will be found that quite a fraction of the gas has been driven into the negative electrode, or into the platinum mirror immediately surrounding it, so that it can not be pumped out. The exact location of the emanation can be most conveniently found by dissecting the tube and examining the various parts for γ radiation.

The Coolidge[2] X ray tube does not depend on ionization by shock, but on the direct production at a highly heated tungsten cathode of enough therm-electrons to carry the current. Consequently the gas pressure in a Coolidge tube may be lowered *ad libitum,* which gives the electrons much longer free paths, resulting in their arriving at the target with very high velocity, producing X rays of much shorter wave length and higher penetrating power. It has not yet been possible to equal γ rays in these respects.

17. Some Properties of β Particles and Electrons.

β particles are electrons emitted from radioactive substances. They differ very markedly from α particles in many respects. Their much smaller mass prevents their carrying the same order of kinetic energy even when moving at velocities approaching that of light. The initial velocities of the various β particles vary from 0.3 to 0.98 of the velocity of light. Like α particles they produce ionization and phosphorescent and photographic as well as chemical effects. The electrical method presents the best means for their study. The idea that formerly prevailed that each radioactive substance emits only a single simple type of β radiation has had to be abandoned in favor of the view that great variations exist with respect to velocity of emission. Coupled with the fact that their ionizing and penetrating properties are highly dependent upon velocity, a degree of complexity and uncertainty is encountered in dealing with β particles which is quite foreign to the exact nature of our knowledge regarding α particles. The apparent mass of the electron

[2] W. D. Coolidge, *Phys. Rev.* (2) 2, 409-30 (1914).

has also been found to vary with its velocity. Kaufmann[3] has made the most exact investigation of this subject.

The absorption phenomena for β rays are also very different from those for α rays. It has already been pointed out that the α particle, while non-penetrating to collective matter owing to the large number of collisions made in a short path, is extremely penetrating with reference to the individual atom, traveling in a straight line through an immense number before its energy is expended. For β particles exactly the opposite is true. To matter collectively they are quite penetrating, because owing to their small size and high velocity they "slip between" the molecules, making a much smaller number of collisions per unit path, but suffer a much greater deflection or scattering for each collision. Consequently the paths by which β particles traverse matter are very far from straight lines; they are even frequently deflected through 180° and return in the opposite direction. This ease of deflection corresponds to the well known ease with which they are deflected by electrical and magnetic fields. Besides the gradual reduction in velocity experienced by β rays similar to that of α rays, it is also probable that at any part of its course a β ray may collide with a molecule in such a way that it is stopped abruptly. This means that instead of all β rays with a given initial velocity traveling the same distance in an absorbing medium, as do α rays, they are gradually absorbed proportionally to the number remaining to be absorbed at any point in the path, which behavior would be expressed by an exponential law. Owing, however, to the various complications which arise through scattering, unequal velocities and other causes, the direct application of an equation of the form: $I=I_0(1-e^{-\mu d})$ is possible only in a few special cases, I_0 being the initial intensity, and I that after the radiation has traversed the thickness d in a medium with an absorption coefficient μ.

Owing to its smaller mass and kinetic energy, a β particle produces much less ionization than does an α particle, 200 fold less on the average per unit path for β particles expelled from radium. The total number of β particles emitted by radioactive substances is not known with the same degree of accuracy as in the case of α particles, but the evidence points to the conclusion that the emission of one β particle per atom decaying is the

[3] W. Kaufmann, *Phys. Zeit.*, 4, 54 (1902).

rule for elements showing β radiation. A very strong piece of indirect evidence in favor of this view is the principle discovered and elaborated by Russell,[4] Soddy,[5] Fajans,[6] v. Hevesy,[7] and others, according to which an element emitting α particles produces an element possessing chemical valence two units less than, and occupying a place in the periodic system two places to the left of, that of the parent element; while an element emitting β radiation produces an element shifted *one* unit in the opposite direction with respect to valence and position in the periodic system. These relations evidently require a unit relationship between the number of atoms changing and the number of α or β particles primarily emitted. Experimental evidence also indicating a number of β particles of that order was obtained by Moseley[8] and more recently by Hess and Lawson.[9] The total number of ions produced in air by the β rays from one gram of radium in equilibrium was found by Moseley and Robinson[10] to be about 9×10^{14} per second, and by the γ rays 13×10^{14} per second. Rutherford[11] estimates for radium in equilibrium that of the total radiated energy, 3.2% is in the form of β rays and 4.7% in the form of γ rays, the balance being represented by α radiation.

The swiftest β rays from Ra C will penetrate in air about 3 m. but are entirely stopped by 2 mm. of lead. Owing to their great range in air and the sparsity of the ionization along their paths, β rays can not be utilized very effectively to produce radiochemical actions in a gaseous system. Their greater absorption in liquids and solids is more favorable for chemical effects.

As in the case of α particles, the ionization produced in gases by β and γ rays has been shown by Millikan and his coworkers[12] to consist in the detachment of one electron from each molecule, leaving a singly charged positive ion.

The subject of the production of ionization by electrons has

[4] A. S. Russell, *Chem. News*, 107, 49-52 (1913).
[5] F. Soddy, "Chemistry of the Radioelements," Pt. II, pp. 16-20 (1914).
[6] K. Fajans, *Phys. Zeit.*, 14, 131 (1913); *ibid.*, 16, 456 (1915).
[7] v. Hevesy, *ibid.*, 14, 49 (1913).
[8] H. G. J. Moseley, *Proc. Roy. Soc.*, 87A, 230 (1912).
[9] V. F. Hess and R. W. Lawson, Sitb. Vienna Acad. IIa, *125*, 661-674 (1916).
[10] H. G. J. Moseley and H. Robinson, *Phil. Mag.* (6) 28, 327-37 (1914).
[11] Rutherford, "Radioactive Substances," pp. 579-80 (1913).
[12] R. A. Millikan and H. Fletcher, *Phil. Mag.* (6) 21, 753 (1911).

already been considered in its qualitative aspects in § 17. The quantitative relations have been most thoroughly investigated by Townsend [13] for ionization produced by electrons of photo-electric origin accelerated by various voltages in an electrical field of definite dimensions. The general equation of Townsend has the form: $n = \frac{n_0(\alpha - \beta)e^{(\alpha-\beta)d}}{\alpha - \beta e^{(\alpha-\beta)d}}$ in which n_0 is the number of ions set free at the cathode, n is the initial number of ions reaching the other electrode if α is the average number of new ions produced per cm. by each negative ion, and β by each positive ion, d is the distance between the electrodes, with the potential X and the gas pressure P remaining constant. When X/P is small the ionization produced by positive ions is sensibly zero and the equation takes the simple form: $n = n_0 e^{\alpha d}$. More recently Horton [14] has proved the applicability of Townsend's equation to *therm*-electrons. Townsend's results show that for a pressure of 1 mm. of air, maximum ionization is attained by increase of voltage when the ionization reaches a value of about 20 pairs of ions per 1 cm. of path.

Recently many investigations have been made to determine the minimum voltage at which radiation and ionization effects begin in different gases, in connection with the application of the quantum theory. Consideration of these results is outside the scope of the present work.

In general it may be pointed out that up to the present, except for the work of Kirkby (see § 52), the chemical effects of the passage of electricity through gases have not been studied under conditions at which Townsend's equations would be applicable, and the total ionization has, therefore, been unknown. Comparison of the amount of chemical action with other factors such as current, voltage, ultra-violet radiation, etc., has not proved very illuminating. It is to be hoped that future work will throw more light upon the fundamental relations involved, through a study of the chemical effects of the passage of electricity through gases under more suitable experimental conditions.

[13] J. S. Townsend, *Phil. Mag.* (6) 1, p. 198 (1901); *ibid.*, 3, 557 (1902); "Theory and Ionization of Gases by Collision" (1910).

[14] F. Horton, *Phil. Mag.* (6) 34, 461-78 (1917).

18. γ Rays and X Rays.

The announcement by Roentgen in 1895 of the discovery of the so-called X or Roentgen rays marked the beginning of a new era in the progress of science. Almost immediately it led to the discovery by Becquerel of the radioactive radiations, which was followed but little later by the discovery of radium by the Curies, and by the rapid development of the subject of radioactivity by Rutherford and Soddy and a host of others too numerous to mention here. It was early found that both X and γ rays possess in common with α and β rays the power of ionizing gases, and of producing photographic and phosphorescent effects. Unlike the two latter, X and γ rays are not deviated by electrical nor magnetic fields, do not carry electrical charge, and are possessed of unusual penetrating powers, in which the γ rays far exceed the X rays.

The electro-magnetic nature of X rays was recognized quite early and they were classified as ether pulses of short wave length having, naturally, the same velocity as light. Although the general similarity between X and γ rays was evident from the first, it was not until much later that it was possible to demonstrate clearly that γ rays are also ether pulses having yet greater frequency and correspondingly shorter wave lengths than X rays.

Not only did the discovery of X and γ rays play an important part in the initiation of the new development in physics and chemistry, but their further investigation has proved extremely fruitful in several directions. The discovery by Laue [15] of the interference principle for X rays and its application by Friedrich, Knipping and Laue [16] to the use of crystals as three dimensional diffraction gratings was shortly followed by the brilliant work of W. L. Bragg [17] on the use of crystals for the specular *reflection* of X rays, which resulted in investigations of fundamental importance both with respect to crystal structure and the nature of X rays.[18] The classical discovery by Moseley [19] of the rela-

[15] M. Laue, *Sitzb. Akad. Wiss. Muenchen,* 1912, pp. 263-73.

[16] W. Friedrich, P. Knipping, and M. Laue, *ibid.,* 1912, pp. 303-22.

[17] W. L. Bragg, "Nature," 90, 410 (1912); *Proc. Camb. Phil. Soc.,* 17, 43-57 (1913).

[18] "X Rays and Crystal Structure," W. H. and W. L. Bragg (1915). W. L. Bragg, *Phil. Mag.* (6) 40, 169-89 (1920).

[19] H. G. J. Moseley, *Phil. Mag.* (6) 26, 1024-34 (1913); 27, 703-13 (1914).

tionship between the X ray spectra of different elements, leading to the establishment of the so-called *atomic numbers,* has opened the way to substantial progress in the solution of the problem of atomic structure. The work of Barkla,[20] Darwin, Sadler, and later of Siegbahn,[21] Duane,[22] Hull,[23] and others on the various types of characteristic radiations from the elements can merely be cited.

Through some of the work on *characteristic* radiations just referred to, Rutherford was led to suspect that the γ rays may be the characteristic radiation excited by the emission of β rays. The plausibility of this hypothesis has been supported from several different points of view until no doubt remains of the existence of this relation of the origin of γ rays from β radiation. This does not mean, however, that a single β ray sets up a single γ ray pulse. As was seen in the preceding paragraph the total ionization by γ rays from radium in equilibrium was found by Moseley and Robinson (*loc. cit.*) to be of the order 13x10[14] pairs per second, about 50% greater than that from the total β radiation.

The most penetrating γ rays traverse several centimeters of lead or several hundred meters of air. In the latter part of the path through lead the absorption becomes exponential in character. Owing to their great penetrating powers it is difficult to utilize γ rays efficiently in the study of radiochemical effects. The subject appears to have great importance, however, since it has been found that it is the physiological effects of the γ *rays* which are utilized therapeutically, but whether or not the effect is produced through the intermediation of chemical action remains as yet wholly unknown. The utilization of the new powerful types of X ray tubes, such as the Coolidge tube (§ 17), also offers an attractive future field for the investigation of radiochemical effects.

[20] C. G. Barkla, *Phil. Mag.* (6) 22, 396-412; *Phys. Zeit.,* 15, 160 (1914).

[21] Manne Siegbahn, *Phys. Zeit.,* 15, 753-6 (1914); *Verh. deut. phys. Ges.* 18, 150-3 (1916); *Nature,* 96, 676 (1916); *Verh. deut. phys. Ges.* 18, 278-82 (1916).

[22] Wm. Duane and Kang-Fuh Hu, *Phys. Rev.* (2) 11, 489 (1918); Duane and T. Shimizu, *ibid.,* 13, 306 (1919).

[23] A. W. Hull, *Am. Journ. Roentgenol.* 2, 893 (1915); *J. Frank. Inst.,* 181, 423.

Chapter 4.

Qualitative Radiochemical Effects.

19. General Classification.

The observation and investigation of radiochemical effects have embraced a fairly broad field with rather undefined boundaries. At the one extreme are those effects of radiation which are not definitely known to be chemical in nature, such as phosphorescence, coloring, and thermoluminescence. Their quantitative aspects from the chemical standpoint have hardly been touched upon. At the other extreme will be found a very limited number of definite chemical reactions which have been found to take place under the influence of α radiation, and which have been very thoroughly investigated both with respect to the nature and amount of the chemical action produced, and also with respect to the amount of radiation producing it, and the mode of the expenditure of the radiant energy in the system acted on. Between these two extremes will be found all degrees of variation with respect to the qualitative or quantitative character of the chemical and radiant factors involved in the reactions studied.

Radiochemical investigations may be arbitrarily classified as follows:

(1) Reactions of doubtful chemical nature which have not yet been thoroughly explained.

(2) Reactions undoubtedly chemical in nature but in which the exact chemical composition of some of the products has not been determined.

(3) Reactions, the chemical products of which have been identified but not quantitatively measured.

(4) Reactions in which the products have been identified and measured but where the quantity of radiation was not known.

(5) Reactions in which the products were identified and

measured and the total quantity of radiation was known, without being able to determine what part of the radiation was effective in the given system.

(6) Reactions characterized by (5) with the additional knowledge of the effective radiation.

(7) Reactions characterized by (6) with complete information as to the kinetics of the reaction from the physical-chemical standpoint.

20. Qualitative Observations.

The observation of some of the remarkable chemical effects of the rays of radium followed very closely upon its discovery. P. and Mme. Curie[1] in 1899 reported the coloration of glass and of porcelain, as well as the formation of ozone from oxygen (observed by Demarcay). F. Giesel[2] found that coloration of the alkaline halides was produced similar to that by cathode rays, and that water is decomposed into its elements. Becquerel[3] showed that the β and γ rays produce many of the reactions that can be brought about by the action of light, such as the change of white to red phosphorus, and the decomposition of hydriodic acid solution and of mercuric chloride. Jorissen and Woudstra[4] showed that the coagulation of some colloidal solutions is caused by the penetrating radium rays. Jorissen and Ringer[5] demonstrated the combination of hydrogen and chlorine gases at ordinary temperature under the influence of the penetrating rays.

21. Coloration and Decomposition of Radium Salts.

Radium salts mixed with barium salts in various proportions undergo spontaneous alterations which are first marked by a change of color from the original pure white to a brownish tint which increases in depth with a rapidity dependent upon the quantity of radium present. This progressive change in color is exhibited very strikingly by $Ba(Ra)Br_2$; if successive frac-

[1] P. and M. Curie, *Comp. rend.* 129, 823 (1899).

[2] F. Giesel, *Verh. deut. phys. Ges.* 2, 9 (1900).

[3] H. Becquerel, *Comp. rend.* 133, 709-12 (1901).

[4] W. P. Jorissen and H. W. Woudstra, *Zeit. Chem. u. Industrie d. Kolloide* 10, 280 (1912).

[5] W. P. Jorissen and W. E. Ringer, Ber. 38, 899 (1905); 39, 2093 (1906); *Arch. Néerland. Sci. Exact. et Nat.* (II) XII, p. 157 (1907).

tions with approximately the same radium content are crystallized daily, it is possible to judge their relative ages during the first few weeks by the depth of color. Hönigschmid[6] has observed that radium salts which have not been heated above 200° C. take on only a weak yellowish or gray color even after several years, while those which are heated to red glow become almost black in one or two days. Since he found the drying to be complete in either case Höenigschmid did not attribute the difference to traces of water of crystallization. (Like the corresponding barium salts, both $RaBr_2$ and $RaCl_2$ crystallize as $RaBr_2.2H_2O$ and $RaCl_2.2H_2O$.) Radium chloride undergoes a similar change in color, which does not appear to develop so rapidly as in the case of the bromide. A further proof of the spontaneous chemical change of radium salts is obtained on dissolving them in water after they have been stored for some time. Solution is invariably accompanied by a more or less copious evolution of gas. On dissolving the chloride in water an odor of Cl and ClO_2 is often perceptible. The dry salt stored in a desiccator also has the odor of free chlorine and of ozone. The nature of the changes produced in the salt itself has not been thoroughly investigated, but it is probable that the larger part of the gas evolution observed on dissolving is due to the release of some hydrogen (and oxygen) produced by the radiochemical decomposition of remaining traces of water. In containers filled with air part of the salt is also doubtless converted into oxyhalide, oxide, and even some carbonate.

It has been shown by P. Curie and Debierne[7] that a vacuum can not be maintained over the solid salts, and that from a solution of radium salts a continuous evolution of hydrogen and oxygen takes place. Ramsay,[8] Debierne,[9] and others found that there is some excess of hydrogen in the gases evolved, which was attributed by Kernbaum[10] to the formation of some H_2O_2 in the solution. It should be pointed out, however, that the rather large excess of hydrogen which accompanies radium emanation in the usual method of collecting it from aqueous solution of radium halides is to be attributed to another cause. The halide

[6] O. Hönigschmid, *Sitzb. Akad. Wiss. Wien*, IIa, 121, 1979 (1912).
[7] P. Curie and A. Debierne, *Comp. rend.* 132, 770 (1901).
[8] W. Ramsay, *J. Chem. Soc.*, Lond., 91_I, 931 (1907).
[9] A. Debierne, *Comp. rend*, 148, 703 (1909).
[10] M. Kernbaum, *Le Radium*, 6, 225-8 (1909),

acid which is also present in the solution is decomposed into hydrogen and free halide. The latter combines with the mercury in the collecting system, leaving the corresponding hydrogen in excess of the oxygen. The rate of the decomposition of water by radium and by radium emanation has been quantitatively investigated by a number of authorities, whose work will be fully reported in subsequent chapters.

It may not be amiss to mention here that the decomposition of H_2O in any form by the α rays renders the practice of sealing radium salts in small tubes for long periods of time a dangerous one unless certain precautions are observed. Accidents involving serious loss of radium have occurred through the explosion of tubes by the accumulated pressure of hydrogen and oxygen. It appears to be dangerous to heat an old tube or to exert any mechanical stress upon it. It is possible that weakening of the glass container by the continued radiant bombardment enhances the danger through devitrification of the glass. A far-reaching disintegration of quartz containers by radium rays has been reported.[11] The principal precaution to be observed in sealing radium salts in glass containers is the thorough dehydration of the salt, which should be accomplished by heating for not less than twenty minutes to a temperature not under 250° C. Preferably, the salt should be raised to a red glow in a quartz dish for a shorter time. A good criterion that a temperature has been reached at which complete dehydration takes place rapidly will be furnished by the character of light emitted by the radium salt after heating. The light should show the intensely blue rather than the ordinary pale yellow luminescence of radium salts. The blue luminescence is a result of the effect of temperature and is not directly connected with the degree of dehydration, since the intense blue light persists even under water as long as any salt remains undissolved. Karrer and Kabakjian[12] have made a study of this blue luminescence and attribute it to the formation of a double salt of radium and barium. This appears difficult to reconcile with Hönigschmid's[13] observation that $RaCl_2$ of the highest purity, prepared for atomic weight de-

[11] Rutherford, "Radioactive Substances" (1913), p. 308. Hönigschmid, *Sitzb. Akad. Wiss. Wien*, IIa, 120, 1624 (1911); St. Meyer and V. F. Hess, *ibid.* 121, 255 (1912).

[12] E. Karrer and D. H. Kabakjian, J. Franklin Inst., 186, 317-40 (1918).

[13] O. Hönigschmid, *Sitzb. Akad. Wiss. Wien*, IIa, 120, 1617-52 (1910).

termination, showed the blue color in a very enhanced degree after fusing. The blue light does not remain constant but dies out rapidly in the course of a few days to a small fraction of the original intensity, but still remains more bluish or lavender than the light from salts which have not been highly heated.

22. Coloration of Glass and Minerals.

The color produced in glass and many transparent minerals by radium rays and other forms of radiation has been a frequent subject of investigation, without the establishment of a final theory of its nature. C. Doelter[14] has devoted a monograph to the experimental and descriptive phases of the subject. Many attempts have been made to find a connection between the color produced and the presence of some constituent of the glass or mineral. Most glasses are colored either violet or brown, and it has been stated that soda glasses take the violet and that potash glasses take the brown shades. Others would attribute the violet to manganese, as appears to be true for the coloration by ordinary light of glass containing manganese. Bancroft[15] has proposed a physical theory depending on the partial coagulation of coloring material in the colloidal state until a particle of a certain size is produced capable of scattering some wave lengths and transmitting others, which coagulating process, he believes, might be stimulated by radiation. Meyer and Przibram[16] found that the photo-electric effect is increased in glass, and more markedly in fluorspar and kunzite, that had been colored by radiation with radium rays, and therefore favored a physical theory of the effect.

It does not appear possible at present to formulate a satisfactory theory of the coloring effects, nor to decide whether they are chemical or physical in nature. Very great difficulties are encountered in trying to ascribe the color to any definite component, though it seems to be rather generally agreed that the presence of impurities, possibly in extremely minute quantity beyond the range of chemical determination, influences the color production. This would be suggested by the erratic differences

[14] C. Doelter, "Das Radium und die Farben" (1910).

[15] W. D. Bancroft, *Jour. Phys. Chem.* 22, 601 (1918).

[16] St. Meyer and K. Przibram, *Sitzb. Akad. Wiss. Wien*, IIa, 121, 1414 (1912).

found for the same mineral from different localities. Goldstein[17] estimates that impurities amounting to not more than one part in a million produce color effects under the influence of cathode rays. The confusion that arises in attempting to settle on some certain component or impurity as responsibile for the color may be illustrated by some of the following observations. Meyer and Przibram (*loc. cit.*) report that they have observed the production of the violet and of the brown color simultaneously on different parts of the *same glass vessel,* which were subjected to a difference only in the intensity of the radiation; while, in general, difference in intensity or even the kind of radiation influences only the rate at which color is produced. An outer glass tube enclosing an inner one (of the same glass) containing radium salt, takes on the same color as the inner one, though more slowly, although the outer one receives no α radiation and a different intensity of penetrating radiation from that received by the inner one. Hard glasses high in silica, of the pyrex or Jena type, invariably take the brown color, but silica vessels, including the transparent variety made from pure fused quartz, take the same violet color as ordinary soft glass. Lead glass is colored brown. In all cases the glass appears finally to become saturated and the color no longer deepens. Thick layers of glass appear to be more intensely colored on account of the depth of layer. Very thick glass, like the walls of a desiccator, becomes almost opaque upon prolonged radiation. The power of luminescing diminishes as the coloring increases. (Mme. Curie, "Radioactivité," II, p. 219 [1910].)

The color produced in glass and minerals by radium rays and by cathode rays can be discharged by heating almost to the softening point of glass. The same color is again restored by renewed radiation, and the cycle may be repeated, apparently indefinitely, without any fatigue effect.

As a result of an extended investigation of the coloring and thermoluminescence produced in artificial salts and natural minerals by various forms of radiation Meyer and Przibram[18] were led to discard definitely the idea of the influence of impurities, and to favor a return to the theory frequently put forward, of colloidal coloring by metallic particles. Attempts to distinguish discrete particles by means of the ultra-microscope were unsuc-

[17] E. Goldstein, *Ann. d. Physik,* 54, 371 (1895) ; "Nature," 94, 494 (1914).
[18] S. Meyer and K. Przibram, *Sitzb. Akad. Wiss. Wien,* 123, 653 (1914).

cessful except in the case already known of the heating of rock salt previously radiated. .

It has been shown by Rutherford[19] and by Joly[20] that the depth of the layer of glass or mineral colored by α rays corresponds to the range of α particles in the given substance. Joly first pointed out that the so-called "pleochroic halos," small dark spots in certain kinds of mica (biotite, cordierite, and muscovite), are due to coloring produced by minute radioactive centers in the mineral. Joly[21] and Joly and Fletcher[22] have made an extended study of the subject, showing that the diameters of the concentric rings constituting the halo correspond to the ranges of the different sets of α particles in the uranium-radium series, and that there is a relation between the development of the halo and the geological age of the mineral.

23. Thermo-luminescence Produced by Radiation.

It has been found by many observers that salts, glass, minerals, and other substances after being exposed to radium or to cathode rays become luminous in the dark at temperatures from 40° to 200° C. This appears to be due to an effect of the radiation which is as yet little understood. The mistake has been rather commonly made of supposing that there is a close connection between the discharge of color produced in glass, for instance (see preceding paragraph), and the thermoluminiscent effect. However, it has recently been pointed out by Lind[23] that thermoluminescence can usually be exhausted at about 200° without at all diminishing the color, which is not discharged from ordinary violet colored glass below 400° to 500° C., so that there is evidently no direct connection between the two effects. Meyer and Przibram[24] have made an interesting observation which has been confirmed by Lind (*lot. cit.*) that if glass colored brown by radium radiation be heated gently until its thermoluminescence is exhausted, its color is changed to the more common violet tint which then behaves as in glass originally

[19] Rutherford, "Radioactive Substances" (1913), p. 307 *et seq.*

[20] J. Joly, *Phil. Mag.* (6) 13, 381 (1907).

[21] J. Joly, "Radioactivity and Geology" (1909), pp. 64-9; *Phil. Mag.* (6) 19, 327 (1910).

[22] J. Joly and A. L. Fletcher, *ibid.*, 19, 630 (1910).

[23] S. C. Lind, *Journ. Phys. Chem.* 24, 437 (1920).

[24] St. Meyer and K. Przibram, *Sitzb. Akad. Wiss. Wien*, IIa, 121, 1414 (1912).

colored violet, except that no further thermoluminescence is exhibited. Upon renewed radiation the color returns to brown.

Freshly radiated glass will show thermoluminescence to the well rested eye at temperatures quite below the boiling point of water, while glass which has been kept for three or four years after exposure must be raised to the neighborhood of 200° before luminescence sets in (Lind, *loc. cit.*).

From the foregoing statements it appears that if the coloration and thermoluminescence of glass and minerals are due to chemical causes, at least two different sets of reactions are involved which may have little or no connection with each other. The whole subject presents an attractive field for further investigation.

Meyer and Przibram (*loc. cit.*) examined the thermoluminescence of a series of artificial borates and silicates of the alkalis, alkaline earths and some other metals. It appeared that the wave length of light emitted by a given group decreased with increasing atomic weight of the metal.

24. Luminescence and Phosphorescence Produced by Radiation.

Certain substances under the influence of various kinds of radiation emit light of visible wave lengths at ordinary and even at extremely low temperatures. The use of phosphorescent zinc sulfide screens to count α particles by means of the scintillations produced was referred to in § 12. The phenomenon of scintillation is not only important as a means of counting the α particles, but historically important as the first experimental evidence of the individual existence of atoms, and also as representative of fluorescence in its simplest form. Scintillations can be individually observed and counted only when the number of α particles falling on a given area of screen in unit time is limited. When the number is greatly increased the screen appears to be uniformly illuminated. In the radium luminous paints, radium salts are intimately mixed with phosphorescent zinc sulfide, which mixture is then applied to a dial or other surface to be illuminated. These luminous mixtures have come into extensive use on watch and clock dials, electric push buttons, etc., and during the War were widely used for illuminating dials on aero-

planes, battleships, or in any place where it was desired to have a feeble light not visible for more than a few yards.

The nature of the reaction furnishing the light is not thoroughly understood. Rutherford[25] has proposed a theory that a phosphorescent substance contains initially a large number of "active centers" or molecular aggregates which are disrupted by α particles with the emission of light. Marsden[26] examined the effect of intense α radiation on phosphorescent zinc sulfide and found that the intensity of the light emitted falls off rapidly. The number of scintillations remains constant, but the light emitted from each scintillation becomes feebler, owing to the gradual exhaustion of the active centers. Rutherford has calculated that a single α particle destroys all the centers in its path within a radius of about 1.3×10^{-7} cm. for ZnS, and about 2.5×10^{-7} cm. for willemite. The decay curves of luminous radium paints such as used by the British Admiralty have been carefully determined by Paterson, Walsh, and Higgins,[27] whose results are not only of great practical but of much theoretical interest. After mixing with a radium salt the luminosity of the paint increases owing to the growth of radium emanation and active deposit; after ten to twenty days this increase is counterbalanced by the decay of the ZnS, so that a maximum is attained. The luminosity then begins to fall, slowly at first and then more rapidly. At the end of six or seven weeks the rate of decrease becomes exponential with the time according to the equation: $B/B_0 = e^{-kt}$, in which B_0 and B are the luminosities initially and at any time t, and k is the decay constant. Between 40 and 200 days the rate of decay follows this law closely, and then becomes slower. After 500 days a practically constant value is attained of about ¼ the luminosity at maximum. Walsh[28] has proposed a "recovery" theory, according to which a state of equilibrium is reached between the two opposing reactions:

$$\text{Decay of active centers} \rightleftarrows \text{Regeneration of active centers.}$$

Walsh established kinetic equations and showed that they fit such an assumption without any hypothesis as to the nature of the two reactions.

[25] E. E. Rutherford, *Proc. Roy. Soc.* 83A 561 (1910).
[26] E. Marsden, *ibid.* 83A, 548 (1910).
[27] C. C. Patterson, J. W. T. Walsh, and W. F. Higgins, *Proc. Phys. Soc.*, Lond. 29, 215-49 (1917).
[28] J. W. T. Walsh, *Proc. Roy. Soc.* 93A 550 (1917).

Both the luminosity and rate of decay of the luminous compounds depend upon the quality of the phosphorescent ZnS and the proportion of radium in the mixture. Evidently it is undesirable to use for any purpose a more luminous paint than is required, both on account of the initial cost of the radium and the shortened life of the compound through more intense radiation. The upper limit of radium is about one part to four thousand of ZnS. Below this, various grades are used down to one part in one or two hundred thousand. The purity of the radium salt employed should be between 10 and 100%. A very interesting fact pointed out by Patterson, Walsh and Higgins (*loc. cit.*) is that the rate of decay and luminosity of a paint are three to four times smaller after application to a dial than before. This is evidently due to the partial absorption of the α radiation by the binding agent used to make the paint adhere to the dial. It is very fortunate that the great loss in luminosity is compensated by a corresponding lengthening of its life.

On account of the long life of radium and the consequent waste in applying it to a dial, the use of which is limited to a few years, it has been proposed [29] that the corresponding member of the thorium series, meso-thorium, should be used, which has a half-period of 6.7 years [30] and would be effective for a period sufficient for all practical purposes. Walsh [31] has discussed the theory of meso-thorium paints and developed the theoretical decay curves. Meso-thorium itself emits no α radiation, which must be generated by the growth of radio-thorium with a half period rate of 1.876 years,[32] which involves the disadvantage of requiring the "ripening" of meso-thorium salts for one or more years before using, but the advantage that, if used before α radiation attains a maximum, its growth will in part compensate the deterioration of the ZnS. It has been reported that the use of radio-thorium for luminous paints has become common in the Swiss watch industry. The parent meso-thorium is employed therapeutically through the use of its γ radiation, and at suitable intervals, a year or two, the salt is put into solution and radio-thorium precipitated for luminous preparations, the meso-thorium being then returned into therapeutic use. It is questionable,

[29] R. B. Moore, *Bull. Am. Inst. Min. Met. Engs.*, Aug., 1918.
[30] L. Meitner, *Phys. Zeit.* 19, 257-63 (1918).
[31] J. W. T. Walsh, *Proc. Roy. Soc.* 93 A, 562-5 (1917).
[32] B. Walter, *Phys. Zeit.* 18, 584 (1917).

however, if the use of such a short-lived product as radio-thorium in the luminous paint industry can be recommended.

The method of preparing phosphorescent zinc sulfide has not been fully described in the literature. Crystalline ZnS (Sidot's blende), also called hexagonal ZnS, can be prepared in a variety of ways. Its phosphorescent qualities vary greatly and appear to depend on at least two factors, the heat treatment and the presence of small quantities of certain impurities. The methods in commercial use have been carefully guarded and it is not possible to give full details. The heat treatment consists in raising the ZnS mixture for a limited time out of contact with air to a temperature at which incipient crystallization begins. The development of large, coarse crystals is to be avoided; on the other hand, the crystalline structure should be distinct after cooling. Fine grinding of the crystals damages their luminescent qualities. The temperature and time of heating will depend to a large extent upon other experimental conditions. 800° to 900° C. at least is necessary for best results though some phosphorescence begins to be developed as low as 600°. 1300° appears to be the upper limit at which favorable results can be obtained. With respect to the impurities necessary there is the widest divergence of views. It has even been claimed that the purest possible ZnS is best. This has been definitely disproved by experiments of C. W. Davis[33] in the laboratory of the U. S. Bureau of Mines. Starting with a very pure zinc spelter and taking great precautions with all the reagents used, it was possible to prepare ZnS of such purity that no heat treatment would develop any phosphorescent properties towards ordinary light and only a faint luminescence under the action of relatively large quantities of radium emanation. The admixtures which have been mentioned as advantageous are manganese, copper, or bismuth salts, sodium chloride, and salts of the rare earths. Chemical examination of some commercial samples of phosphorescent ZnS has failed to disclose the effective impurities and it is quite possible that the quantities required are not chemically determinable. It also appears that neutral salts are sometimes added to "camouflage" the presence of the effective agents.

The properties of phosphorescence toward ordinary light and of response to α radiation are not necessarily coincident, and for

[33] Unpublished results of C. W. Davis.

some interest to touch briefly on some of their general characteristics and to compare them with photochemical reactions. The wide variety of chemical actions brought about, particularly by the α rays, is surprising, and one must be struck by the universality of the phenomenon of chemical change by corpuscular radiation. This is in marked contrast with photochemical action, where the specific nature of the reaction and of the system being acted on depends entirely upon the wave-length of the light, and its capability of being absorbed by the given system. The highly specific and selective nature of photochemical reactions is their chief characteristic; whereas, we find that α and β rays, in their passage through molecules, are almost universally capable of changing them chemically; their action does not depend upon any reciprocal relation with the atom or molecule affected, similar to a resonance effect. Owing to the tremendous kinetic energy of the α particles they always ionize and frequently produce chemical changes in the substances through which they pass. Several different views have been expressed regarding the mechanism of the reactions, which may be classified in general terms as: catalytic, mechanical and electrical. Discussion of the theories will be deferred until after the experimental data have been presented, but it may not be amiss to state by way of anticipation that the evidence supporting an electrical or ionization theory of the chemical effects appears to have much in its favor and will be given full consideration in Chapters 7 to 9.

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Chapter 5.

Chemically Quantitative Investigations in Liquid Systems.

26. Decomposition of Water by Radium Salts in Solution.

The first observations of the decomposition of water by radium in solution were qualitative, as has already been mentioned. As soon as a standard for the measurement of radium was made possible through the researches of Mme. Curie, it appeared to be very simple to measure the amounts of hydrogen and oxygen liberated from solution per unit of radium in unit of time. The wide variations in the values reported by different authorities were sufficient, however, to convince one that the subject was more complicated than was at first anticipated.

Although the decomposition is produced mainly by the α rays, which would be entirely absorbed by very thin layers of water, and which, so far as those from radium alone are concerned, would expend all their energy within the liquid system, additional factors must be considered. In the first place, it was not at once recognized that the decomposition is really due to α radiation. It should be mentioned here and reiterated as later occasions arise, that the first attempts to explain the chemical effects of radium, somewhat naturally but unfortunately, took the uncertain paths of *catalysis,* which was perhaps regarded as peculiarly suited to explain the effects of the radioactive changes, themselves so puzzling to chemists in the beginning. It was not until 1910 that Usher [1] stated that the reactions are due to α rays and can in no sense be regarded as catalytic. This means simply that more definite laws have been established—which may later be accomplished for other classes of reactions now classed as catalytic. (See also § 58.)

The second factor which produced confusion and which goes hand in hand with the failure to recognize that the decomposition is due to α rays, was the false idea that the seat of reaction

[1] F. L. Usher, *Journ. Chem. Soc. Lond.* 97_I, 389-405 (1910).

is confined to the radium in solution; whereas, in reality, radium emanation distributes itself, as would any slightly soluble gas, between the liquid and gas phases in a proportion dependent upon the temperature. The α radiation from the gas phase is much less effective than that in the water, since part of the radiation is absorbed by the walls of the container. In some early experiments a small amount of water was used to hold the radium salt in solution in a relatively large vessel, thus greatly reducing the efficiency of absorption of the radiation by the water to be acted on. Taking into account the partition of the emanation and its active products, it is evident that not only the relative volumes of gas and liquid phases, but also the temperature, the surface of the liquid phase, and the absolute dimensions and the shape of the containing vessel would influence the amount of water decomposed by a given quantity of radium in solution. Neglect of these factors accounts for the wide variations in different observations. Maximum decomposition can be attained only in the absence of any gas phase, which is difficult to realize on account of the evolution of hydrogen and oxygen. These conditions have perhaps never been fulfilled experimentally for a radium solution, but an indirect calculation will give the maximum sought. Duane and Scheuer [2] found for radium emanation in equilibrium with Ra A, B, and C: 2.9 $cm.^3$ (per hour per 1 curie) of electrolytic gas. Assuming that the decomposition produced by the α particles of radium is proportional to the ionization or to the energy absorbed (see Table I, page 28), one calculates for the maximum decomposition of water by a radium solution in equilibrium with Ra A, B, and C: *3.6* $cm.^3$ of hydrogen and equivalent oxygen per hour per gram of radium. Fuller consideration of the results of Duane and Scheuer and of Usher on the decomposition of water by radium emanation will be reserved for the following chapter.

27. Formation of Hydrogen Peroxide in Water.

It has been observed by Runge and Bodländer,[3] Ramsay,[4] Kernbaum,[5] and Duane and Scheuer [6] that the mixture of hydro-

[2] W. Duane and O. Scheuer, *Le Radium* 10, 42 (1913).
[3] C. Runge and G. Bodländer, Ber. 35, 3605 (1902).
[4] W. Ramsay, *Jour. Chem. Soc. Lond.* 91_I, 931 (1907).
[5] M. Kernbaum, *Comp. rend.* 148, 705; *Le Radium* 6, 225 (1909).
[6] W. Duane and O. Scheuer, *Le Radium* 10, 33-46 (1910).

gen and oxygen obtained by the decomposition of water by radium radiation contains an excess of hydrogen. The excess is greater in the early stages of the reaction and has been found to amount to an excess of 36% above theoretical in one case.[6] Kernbaum[7] showed that hydrogen peroxide is formed in the water in an amount equivalent to the deficiency of oxygen in the gaseous mixture. As the quantity of hydrogen peroxide accumulates in the solution a point is reached where its rate of decomposition just balances the new formation, under which condition of dynamic equilibrium the gases evolved would have normal composition. This explains the gradual diminution in the observed excess of hydrogen. It is also conceivable that under a slightly changed condition, such as rise of temperature, decomposition of peroxide might for a time exceed its formation which would result in an excess of oxygen. The decomposition of H_2O_2 is partly spontaneous and partly produced by the radiations (see following section). Kernbaum (*loc. cit.*) reports that the action of the penetrating rays results exclusively in the formation of H_2O_2, the gas evolved being pure hydrogen. Kernbaum found that the energy utilized in the formation of H_2O_2 is about 1/10000 of the total, and Mme. Curie[8] estimates that the available energy from the penetrating radiation is about 1/100 of the total, and that therefore the energy utilization of penetrating radiation is about 1%. Kailan[9] on a similar basis estimates from his results about 1.25%.

28. Reactions Produced by Penetrating Rays.

A method of very general use in the examination of the chemical effects of the rays of radium, particularly in liquid systems, consists in exposing the system to the penetrating rays from a closed preparation of radium, usually sealed in glass. This method has the advantage of great simplicity of manipulation, and of constancy of the source of radiation for any desired length of time. The disadvantages consist in having to use relatively large quantities of radium since only the penetrating rays are available, and in having to be content with only a rough esti-

[7] M. Kernbaum, *Le Radium* 7, 242 (1910).
[8] Mme. Curie, "Traité de Radioactivité" (1910), Vol. II, p. 251.
[9] A. Kailan, *Sitzb. Akad. Wiss. Wien* IIa, 120, 1227 (1911).

mation of the proportion of the radiation that is effectively absorbed.

Experiments of Kailan. A very extensive series of experiments has been carried out with large quantities of radium in the Institut f. Radiumforschung in Vienna by Anton Kailan, who has investigated a large number of inorganic and organic reaction of very varied character.

The decomposition of H_2O_2 [10] was investigated at 13-15° and at 25° in paraffined and in bare glass vessels, and was found to take place approximately according to a first order equation. The temperature coefficient is low, 1.2 per 10° C., which is a property common to most radio- and photo-chemical reactions. The velocity of decomposition was found to increase with the strength of the radium preparations, though not quite proportionately to it.

Using a preparation containing 239 mgs. of radium element, Kailan [12a] was able to confirm Kernbaum's discovery (see preceding section) of the production of H_2O_2 in water.

Kailan also studied the decomposition of the alkaline (Na and K) iodides,[11] and later of the alkaline earth iodides,[12] in aqueous solution, as well as the effect of the penetrating radiation on several other inorganic compounds.[12a] The decomposition was greater for KI than for NaI, and greater for both salts in acid than in neutral solution. The rate of decomposition rises very rapidly with the addition of the first quantities of acid (5×10^{-5} molar doubles the rate), but afterwards the increase is slow for further increase of acid. The decomposition of the iodides also increases with the salt concentration, but far below direct proportionality.

A somewhat puzzling result obtained by Kailan in connection with the decomposition of KI is that the rate in neutral solution has a negative temperature coefficient. An explanation may be sought in the well-known fact that radiochemical reactions usually have either no temperature coefficient or very small ones, which would account for no additional decomposition with increase of temperature. The actual observed *diminution* in rate would then be explained by the ordinary influence of tempera-

[10] A. Kailan, *Sitzb. Akad. Wiss. Wien* IIa, *120,* 1213-28 (1911).
[11] A. Kailan, *ibid.,* 120, 1373-1400 (1911).
[12] A. Kailan, *ibid.,* 122, 787-810 (1913).
[12a] *Ibid.,* 121, 1353-84 (1912).

ture on the reverse reaction between the liberated iodine and alkali. When one attempts, however, to apply the same reasoning to decomposition of KI in *acid* solution, which, according to Creighton and McKenzie,[13] also has a negative temperature coefficient, the explanation becomes more difficult. Kailan favors the view that decomposition of KI is due to the direct decomposition of electrolytically undissociated salt molecules. It appears much more likely that the radiation first acts on water to produce an activated (nascent) form of oxygen which reacts with KI in a secondary reaction.

Penetrating rays were found by Kailan to reduce ferric sulfate in aqueous solution, similar to the action found by Ross[14] for ultraviolet light. The decomposition of KBr solution was found to be 20-100 times less than that of KI under the same conditions. Decomposition of $CaCl_2$ could not be detected. The decomposition of the iodides of the alkaline earths and of magnesium disclosed the same general relations as did the alkaline iodides. No relation between rate of decomposition and molecular weight could be established.

Comparing the effects of the penetrating rays with those of ultraviolet light, Kailan found that a quartz mercury lamp at 8 cms. distance gave the same amount of reaction in periods of time 200-800 times shorter than did preparations of radium containing 80-200 mgs. of element placed directly in the liquid.

Kailan[15] also investigated the effect of penetrating rays on a number of organic compounds and reactions. The inversion of cane sugar was observed and referred to the secondary action of a primary acid formation, which was confirmed by the much smaller effect produced in grape sugar. Ester formation from alcohol and acid is not notably affected by penetrating radiation. The decomposition of esters takes place to some extent, but appears to be more of the nature of a shattering of the molecules than of an ordinary saponification. The conversion of nitrobenzaldehyde into acid was produced at a rate of 10-20 thousand times as slowly as by a mercury arc lamp at 8 cms. Chinon and oxalic, malonic and tartaric acids showed no posi-

[13] H. J. M. Creighton and A. S. McKenzie, *Amer. Chem. Journ.*, 39, 474-93 (1908).

[14] W. H. Ross, *J. Am. Chem. Soc.* 28, 786 (1907).

[15] A. Kailan, *Sitzb. Akad. Wiss. Wien* IIa, *121*, 1385; 2127 (1912); *122*, 881 (1913); *123*, 583; 1427 (1914).

tive effects. The electrical conductivity of fumaric acid is raised and that of maleic acid lowered by penetrating rays, with the difference that the magnitude of the effect is about equal for the two acids with radium rays, but much greater for maleic acid in ultraviolet light. This seems to justify the conclusion that the photo-equilibrium between the two stereo-isomers would differ from that reached under the influence of β and γ rays.

Kailan[16] has also examined the effect of penetrating radiation on chloroform and carbon tetrachloride and compared the effect on the former with that produced by ultraviolet light. The radiation from 80 mgs. of element was allowed to act in the absence of light for about three years. In both cases the chief reaction is through the interaction with oxygen of the air; in the case of chloroform resulting in the formation of hexachlorethane, in the case of carbon tetrachloride in the formation of chlorine, and likewise of hydrogen chloride from the reaction of phosgene, primarily formed, with the water present in the compounds. The total decomposition of 30-45 cm.^{3} of CCl_4 in three years amounted to ½ to ¾%, while about twice this quantity of $CHCl_3$ was changed to the extent of ¼ to ½% in the same time, showing that the absolute quantity of change was of the same order in both cases. Similar effects were produced by ultraviolet light in about 1/300th of the time required for penetrating rays.

The effect of penetrating radiation on toluene, both in the presence and absence of water, has been determined by Kailan,[17] using 80 mgs. of Ra element for a period of two years. The products of reaction in the presence of air were benzaldehyde, benzoic acid, and probably formic acid. In the case of dry toluene, less than ¼% was changed in two years. Effects of the same kind and magnitude could be obtained by 22 hours' radiation with a quartz mercury lamp at 8 cms. The effect of the penetrating rays from 110 mgs. of element in two years on 50 cm.^{3} each of toluene and water produced about three times as much acid as in the case of dry toluene. About 70% of the acid was benzoic, and about 30% formic. Radiation for 22 hours with ultraviolet light produced a little less acid than the two years of penetrating radiation. The products consisted of 44% benzoic, 36% formic, and 20% oxalic acid.

[16] A. Kailan, *Sitzb. Akad. Wiss. Wien* IIa, *126,* 741 (1917).
[17] A. Kailan, *ibid.,* IIa, 128, 831-52 (1919).

Chapter 6.

Reactions Produced by Radium Emanation. (First Experiments.)

29. Radium Emanation as a Source of Radiation.

In most respects radium emanation has advantages over any of the other forms of radioactive matter as a source of radiation in the study of the production of chemical reaction. These advantages have already been considered in some detail in § 14.

The heat evolution from one gram of radium in equilibrium with Ra C has been determined by Meyer and Hess[1] to be 132 small gram calories per hour. The evolved heat is generated by the absorption of the various radiations in the matter through which they pass. Rutherford[2] has calculated the following distribution: α particles (including recoil atoms), from Ra, 25.1 cal.; from Emanation, 28.6; from Ra A, 30.5; from Ra C, 39.4; total *123.6;* β rays from Ra C, *4.3;* γ rays from Ra C, *6.5;* grand total for radium in equilibrium *134.4*. This agrees well with the result of Meyer and Hess obtained under conditions where only 15% of the γ radiation was absorbed.

For radium emanation in equilibrium with active deposit, the total from α rays and recoil atoms would be 109.3, or, including β rays, would be 113.6 cal. These heat emissions can be used in calculating the energy efficiency for any given chemical reaction in which the absorption is complete within the system. In cases of incomplete absorption in the chemical system more roundabout methods of calculating the efficiency must be resorted to.

The total ionization per second produced by radium emanation when mixed with air in cylinders of different sizes may be approximately estimated by means of the empirical formula of Duane and Laborde,[3] which may be written in the form:

[1] St. Meyer and V. F. Hess, *Sitzb. Akad. Wiss. Wien* IIa, 121, 603 (1912).
[2] Rutherford, "Radioactive Substances," p. 581 (1913).
[3] Wm. Duane and A. Laborde, *Le Radium* 7, 162-4 (1910); Duane, *Comp. rend.* 140, 581; 786 (1905).

$X = I\,(max.)/13.5(1-0.572.S/V)$, in which X is the quantity of emanation produced per second by 1 gram of radium, I(max.) is the saturation current in electrostatic units after 3 hours when emanation is in equilibrium with its decay products, S is the inner surface of the chamber in cm.^{2}, and V the volume in cm.^{3}. The conversion factor from gram-seconds to curies of radium emanation is: 1 curie $= 4.795 \times 10^5$ gm.secs. The formula of Duane and Laborde is purely empirical and does not apply accurately, as has been shown by Leaming, Schlundt and Underwood[4] to chambers of volumes or shapes very different from those employed by Duane and Laborde. The ionization produced in gases other than air can also be approximately estimated by applying a correction for the specific ionization of the given gas (Table II).

30. Experiments of Cameron and Ramsay.

In 1907 and 1908 Cameron and Ramsay[5] carried out an extended series of experiments on the chemical action of radium emanation on water and on a number of gases at ordinary temperature. Reactions were chosen that would proceed with a change in pressure at constant volume, by means of which the well-known manometric method of determining velocity of reaction could be applied. Since the quantity of chemical action produced, even by relatively large quantities of emanation, is small, it was necessary to confine the reacting substances in volumes so small (1 to 4 cm.^{3}) that the pressure changes could be readily measured. Although the employment of such small volumes appears disadvantageous from the standpoint of the full utilization of the α rays, the practice is not only justified by the accuracy of the measurement of the pressure changes, but also presents an additional simplification if one wishes to calculate the ionization produced in the gases (see Chapter 8).

The apparatus used by Cameron and Ramsay is shown in Figs. 3 and 3a. The introduction of emanation into the reaction chamber K is effected by means of the Ramsay gas pipette A.[6]

[4] T. H. Leaming, H. Schlundt, and J. E. Underwood, *Tr. Amer. Electrochem. Soc.* 30, 365 (1916).

[5] A. T. Cameron and Wm. Ramsay, *Journ. Chem. Soc. Lond.* 91_{I}, 931; 91_{II}, 1266; 1593; 92_{I}, 966; 992.

[6] Wm. Ramsay, *Proc. Roy. Soc.* 76A, 113 (1905); Trans. 91, 939 (1907).

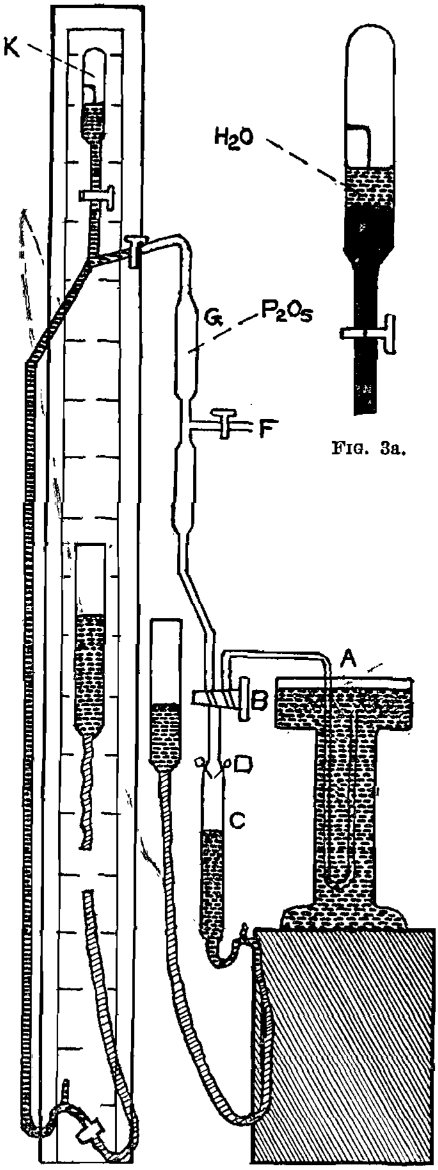

FIG. 3a.

FIG. 3.

The emanation together with the hydrogen and oxygen resulting from the decomposition of the original radium salt solution were collected in vessel C, where the hydrogen and oxygen were removed by means of the spark gap D. After exhausting all the apparatus above the stopcock B through F, the emanation and

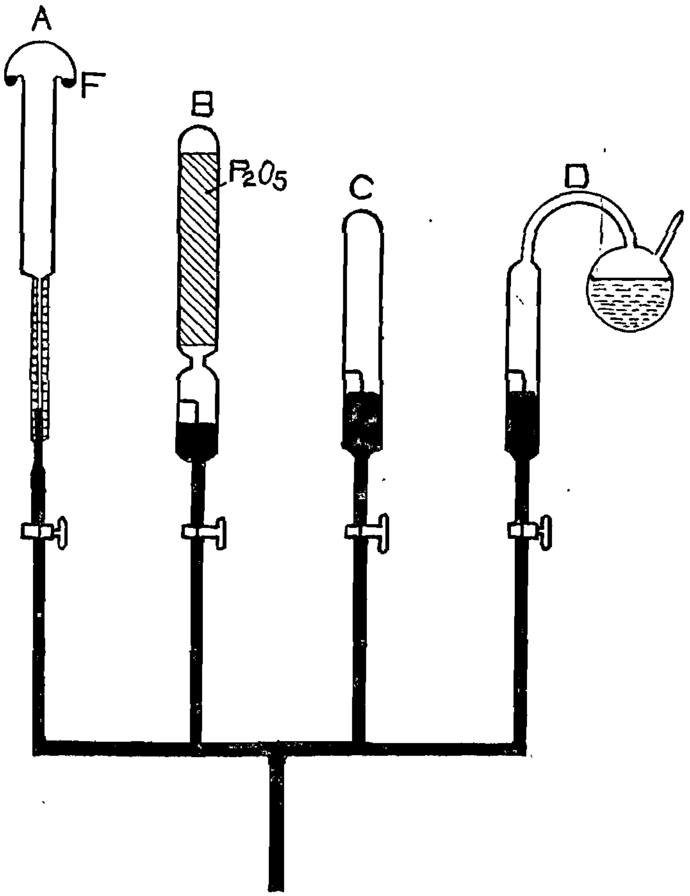

FIG. 4.—VARIOUS REACTION VESSELS OF CAMERON AND RAMSAY.
A. Decomposition of HCl, F, Hg cup; B. combination of H_2 and O_2 (dry); C. combination of H_2 and O_2 (moist); D. decomposition of water.

residual gases were allowed to pass through the P_2O_5 drying bulb G into K. Any gas or gaseous mixture to be investigated was introduced into the reaction chamber in the same way, before the introduction of emanation.

TABLE III

Results of Cameron and Ramsay on the Decomposition of Water by Emanation

Reaction: $(2H_2O) = 2H_2 + O_2$. Water Vol. = 2.302 c.c. Gas Vol. = 3.789 c.c. Ra Em. = 31 milli-curies

Days	Pr. in mm.	Vol. in c.c.	$V\infty - V_t$	$100\frac{V\infty - V_t}{V\infty - V_0}$	% Ra Em left
0.0	39.9	0.200	0.390	100.0	100.0
0.25	42.5	0.212	0.378	96.9	95.6
0.81	49.7	0.248	0.342	87.7	86.4
0.92	52.6	0.262	0.328	84.1	84.8
1.89	62.8	0.310	0.280	71.8	71.4
2.80	71.8	0.358	0.232	59.5	60.5
3.81	80.5	0.401	0.189	48.5	50.6
4.81	86.4	0.431	0.159	40.8	42.2
5.81	90.4	0.451	0.139	35.6	35.2
6.81	90.7	0.484	0.106	27.2	29.5
10.07	107.9	0.538	0.052	13.3	16.4
		(0.590)		0.0	

The experimental arrangement for the measurement of the *decomposition of water is shown in Fig. 3a. The water was introduced immediately over the mercury.* In order to measure several different reactions with the same manometer, the arrangement shown in Fig. 4 was employed, in which the special uses of the various reaction vessels are indicated. Vessel D (Fig. 4) was the form finally adopted for the decomposition of water.

In Table III will be found the data of Cameron and Ramsay's Expt. 3 (*loc. cit.*, p. 973) for the decomposition of water in the apparatus shown in Fig. 4.

$V\infty$, V_t and V_0 are the final, intermediate, and initial volumes respectively. The fraction $100\frac{V\infty - V_t}{V\infty - V_0}$ is the percentage of uncompleted reaction at any time t. The last column shows the percentage of emanation remaining at the corresponding times. The last two columns are in approximate agreement, from which Cameron and Ramsay deduced the general law that the *rate of reaction is always proportional to the quantity of emanation present.* It follows that half of the reaction must be completed in

the half period of emanation, which is 3.85 days. Cameron and Ramsay found the average value of the time required to half complete the reaction in seven different experiments, two for the decomposition of water and five for the combination of hydrogen and oxygen, to be 3.86 days. The law that the rate of reaction is proportional to the quantity of emanation and diminishes at the same rate with its decay can be accepted for a liquid system, as in the decomposition of water, but in a gaseous system in which the pressure changes, it no longer holds except in special cases, as will be shown in Chapter 8. The conclusion of Cameron and Ramsay that "each atom of emanation as it disintegrates produces the same amount of chemical action" is also subject to some modifications. The disintegration is effective in producing chemical action only through the accompanying emission of an α particle. The amount of reaction brought about by each particle will depend upon the length of its path in the gas phase, which will evidently vary for different particles from zero up to the longest path possible in a given vessel, or in large vessels would be limited by the range of α particles in the gas.

In Table IV will be found the data from Cameron and Ramsay's Expt. 4 (*loc. cit.*, p. 974) for the combination of hydrogen and oxygen in the moist gases.

By comparison of the last two columns it will be observed that the rate of chemical action shows a decided tendency to exceed the rate of decay of emanation. This means that the utilization of the α

TABLE IV

Results of Cameron and Ramsay on the Formation of Water by Emanation (Moist)

Volume of Tube 2.186 c.c. Ra Em. 46.5 milli-curies.
Reaction $2H_2 + O_2 = (2H_2O)$

Days	Pr. in mm.	Vol. in c.c.	$V_t - V_\infty$	$100\frac{V_t - V_\infty}{V_o - V_\infty}$	% Ra Em left
0.0	523.5	1.505	0.668	100.0	100.0
1.02	487.0	1.401	0.564	84.4	83.2
2.07	442.0	1.271	0.434	65.0	68.9
3.07	405.6	1.167	0.330	49.4	57.6
4.13	384.5	1.106	0.269	40.3	47.6
4.99	369.5	1.063	0.226	33.8	40.7
6.11	352.2	1.013	0.176	26.3	32.3
7.07	343.5	0.988	0.151	22.6	28.0
9.11	321.4	0.924	0.087	13.0	19.4
10.16	319.3	0.919	0.082	12.3	16.1
11.04	316.6	0.911	0.074	11.1	13.7
12.10	312.3	0.898	0.061	9.1	11.4
97.0	291.0	0.837	0.0	0.0	0.0

form of tube (Fig. 3a, p. 67) was used. In Table V are the results of Cameron and Ramsay for dry hydrogen and

the half period of emanation, which is 3.85 days. Cameron and Ramsay found the average value of the time required to half complete the reaction in seven different experiments, two for the decomposition of water and five for the combination of hydrogen and oxygen, to be 3.86 days. The law that the rate of reaction is proportional to the quantity of emanation and diminishes at the same rate with its decay can be accepted for a liquid system, as in the decomposition of water, but in a gaseous system in which the pressure changes, it no longer holds except in special cases, as will be shown in Chapter 8. The conclusion of Cameron and Ramsay that "each atom of emanation as it disintegrates produces the same amount of chemical action" is also subject to some modifications. The disintegration is effective in producing chemical action only through the accompanying emission of an α particle. The amount of reaction brought about by each particle will depend upon the length of its path in the gas phase, which will evidently vary for different particles from zero up to the longest path possible in a given vessel, or in large vessels would be limited by the range of α particles in the gas.

In Table IV will be found the data from Cameron and Ramsay's Expt. 4 (*loc. cit.*, p. 974) for the combination of hydrogen and oxygen in the moist gases.

By comparison of the last two columns it will be observed that the rate of chemical action shows a decided tendency to exceed the rate of decay of emanation. This means that the utilization of the α rays becomes less complete as the reaction proceeds, owing to the reduction in pressure and consequent diminution in the number of molecules encountered by each particle. Later (see Table XI), cases will be given where larger quantities of emanation are used so that the gas pressure changes through much wider limits, and the discrepancy becomes much more pronounced, showing that Cameron and Ramsay's law is a special case, applying in gases, only when the pressure change is slight. This can be illustrated further by comparison of the last two columns in Table V, in which the amount of emanation used is smaller than in Table IV, consequently the relative pressure change is less and the agreement between per cent of reaction and of emanation decayed is almost as good as in the case for decomposition of water (Table III).

In the experiments just reported with moist gas, the plain

TABLE IV

Results of Cameron and Ramsay on the Formation of Water by Emanation (Moist)

Volume of Tube 2.186 c.c. Ra Em. 46.5 milli-curies.
Reaction $2H_2 + O_2 = (2H_2O)$

Days	Pr. in mm.	Vol. in c.c.	$V_t - V_\infty$	$100\frac{V_t - V_\infty}{V_0 - V_\infty}$	% Ra Em left
0.0	523.5	1.505	0.668	100.0	100.0
1.02	487.0	1.401	0.564	84.4	83.2
2.07	442.0	1.271	0.434	65.0	68.9
3.07	405.6	1.167	0.330	49.4	57.6
4.13	384.5	1.106	0.269	40.3	47.6
4.99	369.5	1.063	0.226	33.8	40.7
6.11	352.2	1.013	0.176	26.3	32.3
7.07	343.5	0.988	0.151	22.6	28.0
9.11	321.4	0.924	0.087	13.0	19.4
10.16	319.3	0.919	0.082	12.3	16.1
11.04	316.6	0.911	0.074	11.1	13.7
12.10	312.3	0.898	0.061	9.1	11.4
97.0	291.0	0.837	0.0	0.0	0.0

form of tube (Fig. 3a, p. 67) was used. In Table V are the results of Cameron and Ramsay for dry hydrogen and oxygen, using the form B, Fig. 4, in which, part of the tube was filled with P_2O_5. No difference was observed by Cameron and Ramsay in the action of emanation on dry or on moist hydrogen and oxygen. This has also been confirmed by Lind.[7]

Cameron and Ramsay (*loc. cit.*) also measured by the same method the effect of radium emanation in decomposing CO_2, CO, NH_3, and HCl gases and in synthesizing NH_3 from its elements. The data for some of these reactions will be presented in Table X, § 42, in a somewhat different connection.

Before passing to other experiments it should be mentioned that Cameron and Ramsay regarded their work as preliminary in nature and it has since been shown[8] that the quantities of emanation reported by them were probably higher than the quanti-

[7] S. C. Lind, *Journ. Amer. Chem. Soc.* 41, 540 (1919).
[8] S. C. Lind, *ibid.* 41, p. 534 and pp. 549-50 (1919).

TABLE V

Results of Cameron and Ramsay on the Formation of Water by Emanation (Dry)

Reaction: $2H_2 + O_2 = (2H_2O)$
Expt. 6 (*loc. cit.*, p. 977). Vol. of Tube 4.996 c.c.
Ra Em. 22.0 milli-curies.

Days	Pr. in mm.	Vol. in c.c.	V_t-$V\infty$	$100\frac{V_t-V\infty}{V_o-V\infty}$	% Ra Em left
0.0	577.6	3.798	0.555	100.0	100.0
1.07	564.1	3.709	0.466	84.0	82.6
1.96	552.4	3.631	0.388	69.9	70.3
2.84	546.9	3.595	0.352	63.4	60.0
3.80	535.6	3.522	0.279	50.3	50.5
4.80	530.2	3.485	0.242	43.6	42.2
6.80	521.5	3.428	0.185	33.3	29.5
9.88	505.6	3.324	0.081	14.6	16.9
11.91	502.8	3.305	0.062	11.2	11.8
13.90	496.4	3.264	0.021	3.8	8.3
21.89	493.3	3.243	0.0	0.0	1.9

ties actually present (§ 44). Nevertheless their pioneer work is of great interest on account of its scope and methods, and represents the first serious attempt to deal experimentally with this very interesting subject.

31. Experiments of Usher on the Ammonia Equilibrium.

In 1910 Usher,[9] working in the laboratory of Ramsay, made an exhaustive study of the decomposition and formation of ammonia by radium emanation. He definitely stated, what Cameron and Ramsay had already considered as possible, that the α particles are the real agents of the reaction, and made the very important advance in recognizing clearly that increase of volume will increase the amount of chemical action produced by a given quantity of emanation through the lengthening of the effective paths of the α rays. Usher calculated that the average number of molecules decomposed by each α particle in a large

[9] F. L. Usher, *Journ. Chem. Soc. Lond.* 97_I, 389-405 (1910).

volume (2 liters) was 134,000, which he estimated to be 90% of the maximum, were all the α particles wholly effective. Through considerations involving ionization Lind[10] used Usher's data in calculating the maximum number of NH_3 molecules that would be decomposed by a single α particle to be 274,000. From more recent experiments of Wourtzel[11] it appears that the number at ordinary temperature must be at least 388,000. The higher efficiency found by Wourtzel for the decomposition of NH_3 by emanation appears to raise some doubt as to the quantity of emanation reported by Usher, similar to the discrepancies attaching to the data of Cameron and Ramsay (§ § 30 and 44).

With respect to the reverse reaction, the formation of NH_3 from its elements, Usher found a reduction in pressure, as had Cameron and Ramsay, but on analyzing the gaseous products, failed to find any certain quantity of NH_3, and concluded that the reduction of pressure was due to some other cause, possibly to the removal of hydrogen by being driven into the glass walls by the α particles. According to Usher, therefore, the equilibrium $2NH_3 \rightleftarrows N_2 + 3H_2$, in the presence of radium emanation at ordinary temperature, lies practically wholly on the side of decomposition of NH_3.

[10] S. C. Lind, *Journ. Phys. Chem.* 16, 603 (1912).
[11] E. E. Wourtzel, *Le Radium* 11, 342 (1919).

Chapter 7.

Relation Between Gaseous Ionization and Radiochemical Effects.

32. Historical Development of the Ionization Theory of the Chemical Effects of Corpuscular Radiation.

In the foregoing chapters the chemical effects of the radiations, particularly of the α rays, of radium have been considered, first in their qualitative and then in their quantitative relationships. The quantitative character of the investigations has extended to the measurement of the chemical change produced, and included a certain knowledge of the quantity of radioactive material causing the change. As has already been pointed out, this knowledge, though important and quite as far-reaching as that possessed in some other branches of radiochemistry, furnishes little information as to the true relation between quantity of radiation and chemical change, since the actual quantity of the former utilized in bringing about the latter was known only very approximately, on account of losses of radiation to the walls of the vessel and other losses difficult to take into account. These difficulties are no greater than are met in dealing with other forms of radiation, and under experimental conditions properly controlled, the difficulties are much less with α radiation from radium emanation than with other forms of radiant energy.

Very definite laws have been established (Chapter 2) for the absorption of α rays in gases by means of a study of the ionization produced. As will be shown in the present chapter, it has proved very instructive to relate statistically the ionization in a given system to the chemical action. It is perhaps a matter of surprise that such comparisons were not made earlier than was the case. It will not be without interest to point out some of the reasons historically. Of course, no such comparisons were possible before the development of the standards and methods of measurement of the radioactive substances involved. And in

the case of radium emanation, its collection and purification are prerequisites. A knowledge of the ionization in air and in other gases and of the distribution of that ionization along the path of the radiant particles was also essential. The chief drawback lay in the fact that the ionization was determined for gaseous systems, whereas the chemical actions were first carried out quantitatively in liquid systems, and a comparison appeared too indirect to have value. Furthermore, the gas reactions which were studied quantitatively were not carried out under conditions from which the ionization could be readily estimated.

In 1907 Bragg[1] first calculated from data of Ramsay and Soddy[2] that the number of molecules of water decomposed was almost exactly equal to the number of ions that would have been produced in air by the emanation employed. Apparently Bragg was not impressed by the equality he found and referred to it as a "curious parallelism in numbers." Mme. Curie[3] stated in 1910 with respect to the decomposition of water by α particles that, "the production of electrolytic gas by radium in solution is of the same order of magnitude as that which one would obtain if the number of molecules of water decomposed by the α rays emitted, were equal to the number of ions which these same rays would produce in air."

In 1910 Le Blanc calculated from Bergwitz's[3a] data on the decomposition of water by polonium, that the saturation current in air measured by Bergwitz for the α radiation, corresponded very closely to the current that would be required by Faraday's law to decompose the same amount of water electrolytically as was decomposed by the α radiation of polonium. While Le Blanc's calculation suffers from the disadvantage of comparing air ionization with water decomposition, yet the recognition of the applicability of Faraday's law to this class of reactions, which Le Blanc very aptly classifies under "electrolysis without electrodes," is of great importance, and it is unfortunate that it was not given greater prominence than scant mention in his Elektrochemie (5th Ed., p. 317). Later Le Blanc[4] published

[1] W. H. Bragg, *Phil. Mag.* (6) 13, 333 (1907).
[2] W. Ramsay and F. Soddy, *Proc. Roy. Soc.*, 72, 204 (1903).
[3] Mme. Curie, "Traité de Radioactivité," Vol. II, pp. 247-8 (1910).
[3a] K. Bergwitz, *Phys. Zeit.* II, 273-5 (1910).
[4] M. Le Blanc, *Zeit. Phys. Chem.* 85, 511 (1913).

in full his calculations from Bergwitz's data on which his statement was founded.

33. Production of Ozone by α Particles.

In 1911 the writer[5] undertook in the Institut für Radiumforschung in Vienna, by measuring the quantity of ozone formed by the action of α rays of radium emanation on gaseous oxygen, to compare the chemical action with the ionization. Instead of adopting the method of Cameron and Ramsay of mixing emanation directly with the gas, purified emanation was introduced into an extremely thin-walled small glass sphere about 1 mm. in diameter. The wall thickness was of the order 0.005 mm. which would be equivalent to about 1 cm. of air in the absorption of α rays, leaving the α rays from Ra C a free path outside the bulb of about 6 cms. By placing a bulb of this kind at the center of a glass sphere of about 12 cms. diameter filled with oxygen, the free path of the α rays is fully utilized without their reaching the wall. The ozone formed was absorbed in neutral KI solution and measured chemically.

The construction of such thin α ray bulbs can not be undertaken by the ordinary glass-blower and will therefore be described in some detail. The first glass vessels thin enough to transmit α rays were used by Rutherford and Royds[6] in their work on the nature of the α particle. They were thin-walled capillary tubes, but since no details of their construction were given, the method of making the thin bulbs was worked out more or less independently by Duane and Lind in the laboratory of Mme. Curie. Thin-walled soft glass tubing of 8-10 mm. diameter is first drawn down in the free blast flame to a diameter of about 1 mm. over a length of 6-8 inches. One end is then sealed and the other attached to an ordinary foot-bellows or other source of pressure. Further manipulation is carried on in a simple furnace consisting of a six inch length of hard glass or quartz tubing of about ¾ inch internal diameter open at both ends. The middle portion of the tube furnace is heated either with a blast lamp, or in the case of quartz with a flame containing some oxygen, and should be provided with an asbestos hous-

[5] S. C. Lind, *Sitzb. Akad. Wiss. Wien IIa*, 120, 1709 (1911); *Monatsh.* 32, 295. *Amer. Chem. Journ.*, 47, 397-415 (1912); *Le Radium* 9, 104-6 (1912).

[6] E. E. Rutherford and T. Royds, *Phil. Mag.* (6) 17, 281 (1909).

ing to retain the heat. The glass tube to be worked is then inserted entirely through the furnace and held by the two projecting ends. The lower temperature of the furnace, as compared with a free flame, is compensated by the higher pressure used in working the glass. Under a suitable pressure the soft tubing is further drawn out until it tapers to a very fine tip which is broken off at the thinnest point capable of being worked. The tip is sealed off without the collection of excess glass by just touching the edge of a very small flame. The tip is then introduced into the hottest zone of the furnace and while blowing strongly into the tube, the expansion of a small bulb on the end can be observed from the open end of the furnace. The bulb must be withdrawn just at the right moment to prevent its blowing out. With some practice, bulbs with walls equivalent to 1 cm. of air for α ray absorption can be constructed which will withstand atmospheric pressure in either direction. The bulb may then be sealed to any glass apparatus by means of the original stem, which should be provided with an in-sealed platinum wire to conduct away the unipolar charge if it is desired to enclose a large quantity of emanation entirely in glass over mercury.

The emanation confined in such a bulb can be determined after four hours by its γ radiation in the usual way.[7] A radiometric method was devised by Lind (*loc. cit.*) for determining the maximum range of the α particles from RaC outside the bulb. It consists in placing the bulb at several known distances above a large ZnS screen in an absolutely dark room and measuring the diameters of the circles of light produced on the screen at different distances. In all cases the range sought is the distance from the bulb to the outer edge of the light circle, which is the hypothenuse of a right triangle of which the vertical distance from the screen and the radius of the light circle are the other two sides. From the relation: $\text{Range}^2 = \frac{\text{diam.}^2}{4} + \text{dist.}^2$, the range can be calculated independently at several different distances, and should agree in all cases. The accompanying Table VI gives the results of a series of such measurements on a tube of about 0.005 mm. wall thickness.

[7] Rutherford, "Radioactive Substances," Appendix A, p. 657 (1913). Makower and Geiger, "Practical Measurements in Radioactivity," p. 106 (1912). S. C. Lind, *Journ. Indus. Eng. Chem.*, 12, 472 (1920).

TABLE VI

Radiometric Measurement of the Free Range of α Particles from Ra C Outside a Thin-walled α Ray Bulb

Dist. from Screen	Diameter of Light Circle	Max. Range
cms.	cms.	cms.
5.8	2.5	5.9
5.4	5.0	5.9
5.0	6.4	5.9
4.5	7.3	5.8
4.1	8.5	5.9
3.3	10.0	6.0
		Average 5.90 ± 0.03 cm.

Before undertaking measurements depending on such feeble luminosity the eye should be rested for thirty minutes in the dark. Readings should be made with a feeble ruby light. The diameter of the light circle is most conveniently determined by using steel calipers with sharp points which can be used to scratch the surface of the ZnS, producing a momentary spark which serves to locate the boundaries of the light circle.

The object of obtaining the air range of α rays outside the bulb is to enable the calculation of the ionization produced in the oxygen. The quantities of emanation employed in the ozonization, 25 to 60 millicuries, produce an ionization far too intense to be measured by the saturation current method (§ 15). By referring to the range of α rays from emanation and Ra A (Table I) and to the ionization produced by them and by Ra C along their paths (Fig. 1), and correcting for the specific ionization of oxygen compared with air (Table II), the total ionization can be calculated. One additional correction, however, is necessary, since the α particles pass through the thin glass wall at all possible angles, one must correct for the obliquity of incidence. This was done by a graphical method.

The total number of α particles emitted by a certain initial quantity of emanation through a given time interval may be calculated in two slightly different ways, both mathematically

identical in principle. The average effective emanation E over a time interval t is: $E = \frac{(E_0 - E_t)}{\lambda t}$, in which E_t may be found at any time t by consulting the Kolowrat Table (Appendix, Table A), and λ is the decay constant for radium emanation equal to 0.0075 hr^{-1} or 0.1800 day^{-1}. The average value E in terms of curies then need only be multiplied by the total number of seconds and by the number of α particles emitted per second, originally measured as 3.4×10^{10} in terms of the Rutherford radium standard, which becomes in terms of the International standard 3.57×10^{10}, or for all three sets, including emanation and Ra A and C 10.71×10^{10} α particles per second. Hess and Lawson[8] have recently determined a higher value 3.72×10^{10}, which has been adopted for all calculations in the present work.

The more direct method of calculating the total number emitted is to take into account the quantity of emanation decaying in the given time interval by reference to the Kolowrat table, and multiplying the quantity by the total number of particles emitted by 1 curie of emanation in its complete disintegration, 1.78×10^{16} for a single set of α particles, according to Hess and Lawson. For three sets (emanation in equilibrium): Total $\alpha = 5.34 \times 10^{16} . E_0 (1 - e^{-\lambda t})$.

The purification of the emanation used was by a chemical method developed in the Curie laboratory consisting in the removal of hydrogen and oxygen by means of copper and copper oxide heated externally in the glass tube leading from the radium solution to the small bulb. In the same way organic gases coming from stopcock grease were oxidized by passing over hot $K_2Cr_2O_7$ (or better $PbCr_2O_7$), the products of the two combustions being absorbed by P_2O_5 and fused KOH (or soda lime). Final purification was made by freezing the emanation in a side tube immersed in liquid air while pumping off the residual gases. The emanation is finally confined by mercury in the small α ray bulb so as just to fill it. From radiation considerations it is essential that the mercury shall stand at all times just at the neck of the thin bulb. In using the same apparatus for the combination of hydrogen and chlorine (see p. 119) H. S. Taylor[9] has added a very ingenious regulator to insure this condition.

[8] V. F. Hess and R. W. Lawson, *Sitzb. Akad. Wiss. Wien* IIa, 127, 405-57 (1918).

[9] H. S. Taylor, *Journ. Amer. Chem. Soc.* 37, 24-38 (1915).

The quantities of ozone found in the different experiments were not concordant, but it was very apparent that the order of magnitude of the total number of ions and of ozone molecules is the same. The experiment in which the maximum quantity of ozone was determined was one in which the average emanation was 58.5 milli-curies acting over 5.0×10^4 secs. in which time 8.4×10^{13} α particles were emitted producing 2.6×10^{19} pairs of ions, and 1.4×10^{19} molecules of O_3. Using the more recent data of Hess and Lawson for the number of α particles emitted, the ionization becomes 2.8×10^{19}, and the ratio of the number of pairs of ions (N) to the number of ozone molecules (M) is exactly 2.0, which would be required according to Faraday's law for the formation of ozone electrolytically. The justification for giving most weight to the experiment in which the maximum quantity of ozone was found lies in the fact that the lower values were probably due to losses before chemical measurement, perhaps through traces of mercury in the ozonizing chamber. This experiment in the ozonization of oxygen constituted the first direct comparison of ionization and chemical effect where both were referred to the same gaseous system. A strong confirmation of the result is furnished by the work of Krüger,[10] who studied the formation of ozone by electronic discharge (Lenard rays) and obtained results similar to those for α rays, drawing the conclusion, however, that *one pair* of ions is involved in the formation of each ozone molecule.

The formation of ozone outside a thin α ray bulb containing even a few millicuries of emanation is continuously perceptible by its odor. The same is true in the immediate neighborhood of a strong radium preparation or any other source of intense α radiation. From the results reported in the foregoing parts of this paragraph, it appears fairly certain that ozonization by α radiation and by electronic discharge is an electrical process intimately connected with ionization of oxygen. Present data are hardly sufficient to establish the exact mechanism of the reaction, although a number of attempts have been made in this direction. It is not necessary that the electrical quantities involved should be the same as in electrolysis, since the work of J. J.

[10] F. Krüger, *Phys. Zeit.*, 13, 1040-3 (1912); *Nernst Festschrift*, pp. 240-51 (1912).

Thomson[11] has shown that the varieties of gaseous oxygen ions is much greater than those known in solution. It would be somewhat simpler to propose a theory on the basis of one molecule of ozone per each pair of ions, than for two pairs, and as Millikan, Gottschalk and Kelly[12] have shown, the ionization of some common gases, including oxygen, by α rays results in the removal of but one electron from a molecule. The writer[13] proposed a very general theory based upon the formation of cluster ions around a charged atom or molecule, which upon being electrically neutralized would break down to the highest stable polymer, in the case of oxygen, ozone. Recent work of Loeb[14] and of Wellisch[15] has cast doubt upon the existence of such cluster ions.[16] Various possible mechanisms for the formation of ozone have been formulated by Strong[17] and by Rideal and Kunz.[18] The present experimental evidence hardly appears sufficiently exact to decide in favor of any particular theory. Wendt and Landauer[16] have discussed fully the possibilities in connection with the formation of triatomic hydrogen.

34. Other Gas Reactions.

The apparently close relation between gaseous ionization and ozone formation rendered it very desirable to see if a similar relation holds for other gas reactions produced by α radiation. The extensive data of Cameron and Ramsay were available for the comparison provided a method could be devised of calculating the effective ionization in the vessels used. Since the volumes used were very small the α particles in all cases completely traversed the gas space, and in most cases the paths would be limited to the first one or two centimeters from the point of origin, in which the ionization remains constant along the path, which presented an additional simplification. The problem seemed to

[11] J. J. Thomson, "Rays of Positive Electricity" (1913). *Phil. Mag.* (6) 21, 239 (1911).

[12] R. A. Millikan, V. H. Gottschalk and M. J. Kelly, *Phys. Rev.* (2) 15, 157 (1920).

[13] S. C. Lind, *Amer. Chem. Journ.*, 47, 414 (1912).

[14] L. B. Loeb, *Phys. Rev.* (2) 8, 633 (1916).

[15] E. M. Wellisch, *J. Franklin Inst.* 184, 775 (1917).

[16] G. L. Wendt and R. S. Landauer, *Journ. Amer. Chem. Soc.* 42, 944 (1920).

[17] W. W. Strong, *Amer. Chem. Journ.* 50, 100-31 (1913).

[18] E. K. Rideal and J. Kunz, *Journ. Phys. Chem.*, 24, 379-93 (1920).

be then to find a solution for the average path proceeding in a straight line from any point within a given volume or any point on the inner surface in any direction until again encountering the wall. For any volumes except spherical ones the mathematical problem is one of great difficulty as will be seen in the following section.

35. Calculation of the Average Path of α Particles.

In 1912 the solution of this problem was undertaken by Lind[19] for the sphere. It was established that the average path is a constant fraction of the radius for a sphere of any size. The numerical value of the fraction was found by applying the general formula, at first to ten, and later to one hundred spheres dividing the spherical volume into 100 equal parts. A. C. Lunn[20] has pointed out that an error was made in using the plane instead of the solid angle (ϑ) Fig. 5. The expression according to

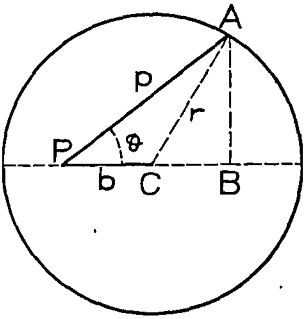

FIG. 5.

Lunn for a sphere is the following. If p be the average path for all α particles originating at any point P within the sphere and traveling to the wall in a straight line PA at any solid angle ϑ with the line PCB through the center of the sphere, where b is any given distance from the center, and μ is the ratio b/r,

$$p = 1/2 \int_0^{\pi} [b\cos\vartheta + r\sqrt{1 - b^2/r^2 \sin^2\vartheta}]\sin\vartheta \, d\vartheta.$$

[19] S. C. Lind, *Journ. Phys. Chem.*, 16, 567 (1912).

[20] Private communication from Prof. A. C. Lunn, Ryerson Physical Laboratory, University of Chicago.

$$p = 1/2 \int_{-1}^{+1} [bx + r \sqrt{(1 - b^2/r^2)(1 - x^2)}]\, dx.$$

Finally for given b: mean $p = \frac{r}{2} \left\{ 1 + \frac{1 - \mu^2}{2\mu} \log \frac{1 + \mu}{1 - \mu} \right\}$

For b = 1, p = *0.5r.* Lunn's integral for the whole spherical volumes gives: p = *0.75r.* Taking into account that in small spheres the induced activity is deposited on the wall and therefore the α particles for Ra A and C originate from the wall, half of them being immediately lost in the wall, while the radium emanation is distributed as gas throughout the volume, the average path of all three sets of α particles from emanation in equilibrium will be: p = 1/3 (0.75 + 2 x 0.5). r = *0.5833 r.*

For volumes other than spherical the problem becomes mathematically far more difficult. From the use of graphical methods the writer concluded that the average path in cylinders in which the length does not exceed the diameter by more than a few fold of the diameter would be approximately the same fraction of the radius of the sphere of equal volume as if the volume were spherical.[21] In all future work it will be advisable to use *spherical* vessels in order to simplify the calculation of the ionization. Some work has already been carried out in spheres by the writer which is reported in Chapters 8 and 9. The whole question of the calculation of ionization in vessels of different shapes and sizes is one worthy of further research. The work of Flamm and Mache [22] on the quantitative measurement of emanation in plate condensers with guard-ring has a bearing upon the subject, but is not directly applicable to radiochemical experiments. The empirical formula of Duane and Laborde was given in § 29, but is not applicable to small volumes.

36. Results of Various Investigations.

By use of the method of calculating ionization by means of the average path of the α particles the experiments of Cam-

[21] Prof. Lunn is extending his calculations to other geometrical forms than the sphere and is convinced that the average path in cylinders of length ten times the diameter will be sufficiently different from that in the sphere of the same volume to be easily tested experimentally. Prof. L. D. Roberts of the Colorado School of Mines has begun an experimental test.

[22] L. Flamm and H. Mache, *Sitzb. Akad. Wiss. Wien* IIa, *121*, 227 (1912); *122*, 535; 1539 (1913).

eron and Ramsay and of others become available for at least an approximate comparison of the electrical and chemical effects. Other methods more or less indirect have been devised for attaining the same end. Duane and Scheuer[23] employed large quantities of emanation in thin-walled capillaries. After measurement of the chemical effects the tubes were held until the emanation had died to such a low value that saturation current measurements could be applied even to the α radiation. Correction had to be made for the growth of polonium during this period and also for the ionization due to penetrating radiation. Scheuer[24] for large bulbs used the empirical formula of Duane and Laborde[25] and corrected for the specific ionization of the gases employed. Wourtzel[26] employed still another method, extrapolating from smaller volumes up to those at which absorption and ionization reach a maximum, in order to use the value for total ionization of the whole α particle in the given gas.

At the end of this paragraph will be found Table VII, in which all the experimental data available for the comparison of chemical effect and ionization have been collected. The application of the "average path" method to the results of Cameron and Ramsay is not strictly accurate on account of the departure of the volumes from the spherical, but it is unlikely that the errors thus introduced are so great as the uncertainty attaching to the quantities of radium emanation reported in the earlier experiments. Many of the experiments summarized in this table will be given detailed consideration in subsequent paragraphs (see accompanying cross-references). The data from work prior to 1911, although unreliable in some respects, have been included either for the sake of comparison with the later work, or because they represent for some reactions the only results available. Repetition of the earlier work should be undertaken where it has not already been done.

A general discussion of the $^{M}/_{N}$ values will be found in §§ 48-50.

[23] Wm. Duane and O. Scheuer, *Le Radium* 10, 33-46 (1913).
[24] O. Scheuer, Comp. rend. 159, 423-6 (1914).
[25] Wm. Duane and A. Laborde, *Le Radium* 7, 162-4 (1910).
[26] E. E. Wourtzel, *ibid.* 11, 289-98; 332-47 (1919).

TABLE VII[27]

I. Gaseous Systems

Statistical Comparison of Ionization and Chemical Action by α Particles

N = Total Pairs of Ions. M = Total Number of Molecules.

Reaction		*Data of*	*Chem. Action Designation of M.*	*M/N*	*% Energy Utilized*
$2H_2 + O_2 = (2H_2O)$	(Moist)	C. & R.	M_{H_2O}	0.65 to 0.81	4.9
"	(Dry)	"	"	0.52 to 0.93	——
"	(130° C.)	"	"	1.59	——
"	(Dry or moist)	S.[29]	"	3.7	——
"	"	L.[31]	"	4.0	34.5
$(H_2S) = H_2 + (S)$		W.[32]	M_{H_2S}	2.65	6.7
$2CO_2 = 2CO + O_2$		C. & R.[28]	M_{CO_2}	0.38	2.6
"		W.[32]	Very small quantity of decomposition.		
$2NH_3 = N_2 + 3H_2$		C. & R.[28]	M_{NH_3}	0.25	——
"		U.[33]	"	0.40	——
"		W.[32]	"	0.80 at 18° 2.55 " 315°	1.2 ——
$2HCl = H_2 + Cl_2$		C. & R.[28]	M_{HCl}	0.76	1.8
$N_2 + 3H_2 = 2NH_3$		"	$M_{(N_2 + H_2)}$	0.25	0.6
"		U.[33]	Very little ammonia formed (chem. anal.)		
"		W.[32]	" " " " " "		
$H_2 + Br_2 = 2HBr$		L.[34]	M_{HBr}	0.54	0.5
$3O_2 = 2O_3$		L.[35]	M_{O_3}	0.50	2.0
$2CO = CO_2 + (C)$		C. & R.[28]	M_{CO}	1.86	3.9
$N_2O = N_2 + O$ or $= (N + NO)$		W.[32]	M_{NO}	1.74 at 18° 2.16 " –78° 2.32 " 220°	4.0 —— ——
$2H_2O = 2H_2 + O_2$		C. & R.[28]	M_{H_2O}	Very little action.	
"		D. & S.[36]	"	" " "	
$H_2 + Cl_2 = (2HCl)$		B. & T.[37]	$M_{(H_2 + Cl_2)}$	4000.	——
"		J. & R.[38]	"	100–1000	——

II. Liquid Systems

Reaction	*Data of*	*Chem. Action Designation of M.*	*M/N*	*% Energy Utilized*
$(2H_2O) = 2H_2 + O_2$	D.[39]	M_{H_2O}	(0.16)	(1.0)
"	C. & R.[28]	"	0.36	——
"	U.[40]	"	0.41	——

TABLE VII—*Continued*

Reaction	*Data of*	*Chem. Action Designation of M*	*M/N*	*% Energy Utilized*
$(2H_2O) = 2H_2 + O_2$	D. & S.[36]	M_{H_2O}	0.86 to 1.05	6.4
$2HBr = H_2 + Br_2$	L.[34]	M_{HBr}	2.6	2.2
KI (in acid soln.) = $(I + K^+)$	"	M_{KI}	0.76	——
		III. Solid Systems		
Ice $(2H_2O) = 2H_2 + O_2$	D. & S.[36]	M_{H_2O}	0.05	0.3
$(KI) = K + I$	L.[41]	Very little decomposition observed for penetrating rays.		
$(PbI_2) = Pb + I_2$	"	" " " " " " "		
$(PbCl_2) = Pb + Cl_2$	"	" " " " " " "		
$(PbBr_2) = Pb + Br_2$	"	No decomposition observed for penetrating rays.		

[27] Table VII is corrected and extended from table of Lind, *Journ. Phys. Chem.* 16, p. 589 (191[illegible]

[28] A. T. Cameron and Wm. Ramsay, *Journ. Chem. Soc. Lond.* 93, 965 (1908). See §§ 29 and 30.

[29] O. Scheuer, *Comp. rend.*, 159, 423 (1914). See § 38.

[30] Wm. Duane and A. Laborde, *Le Radium* 7, 162 (1910). See § 29.

[31] S. C. Lind, *Journ. Amer. Chem. Soc.* 41, 531 1919). See §§ 42, 44.

[32] E. E. Wourtzel, *Le Radium* 11, 289; 332 (1919). See § 39.

[33] F. L. Usher, *Journ. Chem. Soc. Lond.* 97_I 389 (1910). See § 31.

[34] S. C. Lind, *Le Radium* 8, 289 (1911).

[35] S. C. Lind, *Sitzb. Akad. Wiss. Wien* IIa, 120, 1709 (1911); *Amer. Chem. Journ.*, 47, 397 (1912) See also § 33.

[36] Wm. Duane and O. Scheuer, *Le Radium* 10, 33 (1913). See § 37.

[37] (M. Bodenstein) and H. S. Taylor, *Journ. Amer. Chem. Soc.* 37, 24 (1915); 38, 280 (1916). Bodenstein, *Zeit. Elektrochem.* 22, 53-61 (1916). See also § 55.

[38] Jorissen and Ringer, Ber. 39, 2093 (1906). Compare Lind, *J. Phys. Chem.* 16, 610.

[39] A. Debierne, *Comp. rend.* 148, 703 (1909).

[40] F. L. Usher, *Jahrb. d. Radioakt. u. Elektr.* 8, 323 (1911). See § 47.

[41] S. C. Lind. *Journ. Phys. Chem.* 16, 608 (1912).

37. Reactions in Liquid Systems—Results of Duane and Scheuer on the Decomposition of Water, Ice and Water Vapor.

As may be seen from Table VII, the M/N ratio appears to be of the same order in the few liquid reactions that have been investigated as in the majority of gas reactions. From the chemical point of view this may be regarded as a matter of some surprise, but so far as the ionization is concerned, it has been found that variation of pressure of a gas results only in shortening the range of the α particle without affecting the total ionization produced. There is no apparent reason why this should not continue to be true on passing to very high pressures and over into the liquid state. The general assumption has therefore been made in the calculations involved in Table VII that the total ionization by the complete absorption of α radiation is the same as would be produced if the total absorption of the α particle occurred in the same substance in the gaseous state. Owing to the lack of suitable experimental methods of determining the ionization produced in liquids by radiation, it has not been possible to put this conclusion to the test, but if the generality of the equivalence between chemical effects and ionization be conceded, then the evidence of Table VII for liquids constitutes a confirmation of the ionization relations assumed, at least within very approximate limits.

The work of Duane and Scheuer (*loc. cit.*) carried out in the laboratory of Mme. Curie on the decomposition of water in its three states of aggregation is one of the most careful and complete researches in the field of radiochemistry. The experimental method for the liquid and solid states consisted in collecting purified emanation in a thin capillary glass tube (§ 33) in which it was allowed to act upon a layer of water or ice sufficient to absorb the α radiation completely. The quantity of hydrogen and oxygen liberated was measured in a eudiometer tube and the excess of hydrogen was determined after sparking the mixture. By comparing the rate of reaction with the decay curve for emanation it was found that the two coincide perfectly if the volume of gas liberated is corrected for the oxygen retained as H_2O_2, which was measured chemically and found to correspond to the excess of hydrogen. The conclusion was drawn that

water is decomposed in a primary reaction and that H_2O_2 is formed by the secondary action of nascent oxygen on water. A very interesting confirmation of this view was obtained in the examination of the gases liberated by the action of α rays on ice at —183° C., which were found to consist wholly of electrolytic gas, indicating that ice at this temperature is not acted on by nascent oxygen to form H_2O_2.

The comparison of the electrical and chemical effects was made by allowing the emanation to decay to a value where the saturation current method could be applied directly. The original quantity of emanation was calculated from the decay law. The number of gas molecules formed from water is *1.06* times the total number of pairs of ions that would be formed in air in the total absorption of the α radiation. Or expressed a little differently, the α rays capable of producing an ionization current of one ampere in air will decompose water giving 0.1594 cm.$^3H_2$ and 0.0797 cm.$^3O_2$, values of the same order as 0.125 cm.$^3H_2$ and 0.0615 cm.$^3O_2$ which would be liberated per ampere-second in electrolysis. In Table VII the M/N value calculated from the results of Duane and Scheuer is for ionization in H_2O instead of in air, taking the value for the total specific ionization of H_2O as *0.82* that of air.

The action of α rays on ice and on water vapor is much less efficient than on liquid water, not more than 5% as much reaction being found *in maximo.* In the case of water vapor the emanation was mixed directly with the vapor at three atmospheres pressure at 170° C.; the excess of hydrogen amounted to about 50%. Duane and Scheuer express the opinion that the low efficiency of the action of α rays on water vapor is due to recombination of the products.

In Table VIII will be found the results of Expt. III from Duane and Scheuer (*loc. cit.*). Two additional columns have been added to show the course of the reaction compared with the decay of emanation. It will be noticed that the reaction runs slightly behind the decay of emanation, but if correction be made for the deficiency of oxygen according to the excess of hydrogen, the agreement is within a few tenths per cent in nearly all cases. The most probable value for the decomposition of water by emanation is 390 cm.^{3} of electrolytic gas per curie.

TABLE VIII

Decomposition of Water by Emanation according to Duane and Scheuer

Initial Emanation 191.5 milli-curies.

Days,	*Hrs.*	H_2+O_2 *in c.c.*	*% Excess H_2 by Vol.*	*% Reaction Completed*	*% Emanation Decayed*
0	16	0.1730	....	10.1	11.3
1	16	0.4061	16.1	23.9	25.9
3	16	0.7903	8.55	46.2	48.4
4	16	0.9314	....	54.4	56.8
5	16	1.0574	....	61.8	63.9
6	16	1.1501	6.90	67.2	69.9
7	16	1.2372	....	72.3	74.8
8	16	1.3149	....	76.9	79.0
10	16	1.4385	4.96	84.0	85.3
17	16	1.6224	....	94.9	95.8
22	20	1.6690	2.77	97.5	97.9
32	16	1.7071	1.74	99.7	99.7
48	20	1.7099	0.48	100.0	100.0

It may be pointed out that the use of thin-walled α ray bulbs excludes the participation of recoil atoms in the reaction, since they do not penetrate the wall. (See § 64.)

Duane and Scheuer saw in the equivalence between the ionization produced by α particles and the decomposition of water "a coincidence having a profound significance in the theory of electrolysis and the decomposition of matter by the α rays of radium."

38. Experiments of Scheuer on the Formation of Water by α Radiation.

The very careful work in the Curie Laboratory on the chemical effects of radium radiation was extended by Scheuer[42] to the formation of water from its elements. In order to utilize the α rays as fully as possible Scheuer employed rather large glass spheres in which emanation was mixed with electrolytic

[42] O. Scheuer, *Comp. rend.* 159, 423-6 (1914).

mixture of hydrogen and oxygen under increased pressure. After the lapse of several days to a month the quantity of reaction was determined by analyzing the gases. In all cases Scheuer reported the formation of some H_2O_2, which in one case represented 16% of the combined hydrogen. Two experiments were made using α ray bulbs at the center of the gaseous mixture. The ionization was calculated by means of the Duane and Laborde formula (see § 29), but since this is directly applicable only to air, some correction for specific ionization of electrolytic gas must have been made. The M/N values for four different experiments are very concordant between 5.40 and 5.61 with an average of 5.51, where M refers to the total number of $2H_2 + O_2$ molecules combining, which is equivalent to 3.7 molecules of water formed (disregarding H_2O_2 and treating the entire reaction as water formation). This value, though much higher than the older ones of Cameron and Ramsay (see Table VII), agrees fairly well with the more recent one of Lind (*loc. cit.*) 3.9 (or 4.0 using Lunn's value of average path and Hess and Lawson's value for number of α particles and making a slightly different assumption as to the position of Ra A in the reaction bulb).

In the two experiments where Scheuer used α ray bulbs at the center of his mixture he still employed the formula of Duane and Laborde to calculate ionization, although it is inapplicable, as he realized. By confining all the emanation at a point source in the center, the full radius of the sphere is utilized, instead of the average path, which is equal 0.5833 x radius (see § 35). By multiplying Scheuer's values for $\frac{M_{(H_2+O_2)}}{N}$ (8.08 and 8.88) by this value, one obtains 4.7 and 5.1 in fair agreement with his other values reported above. Scheuer also carried out one experiment with oxygen mixed with emanation but found very little ozone under his experimental conditions. For further consideration of Scheuer's results in another connection see § 43.

Scheuer[43] also investigated the reduction of CO by H_2 in the presence of radium emanation, which reaction had already been studied under somewhat different conditions by Stoklasa, Sebor and Zdobnicky,[44] who found formaldehyde to be one of

[43] O. Scheuer, *Comp. rend.* 158, 1887-9 (1914).
[44] J. Stoklasa, J. Sebor and V. Zdobnicky, *ibid.,* 156, 646-8 (1913).

the products of reaction. This was confirmed by Scheuer, who reported, however, that the final product is mainly CH_4.

Equilibrium between Hydrogen and Oxygen mixed with Emanation. Although this subject was not treated by Scheuer, it is very appropriate to consider it in connection with his results on the formation of water and those of Duane and Scheuer (*loc. cit.*) on its decomposition. Since Duane and Scheuer showed that the decomposition of water vapor is very slight, we should expect that the homogeneous gaseous equilibrium would lie quite far on the side of combination. No direct experiments have been made on the subject. In the case of the heterogeneous equilibrium between hydrogen and oxygen and such small quantities of water as could result from the combination of electrolytic gas in small volume at pressures not excessive, the solubility of emanation in the water phase may be neglected, and we should expect equilibrium near 68% of combination (on the basis of M/N for formation = 4, and for decomposition M/N = 1), *provided* that the condensed water is so distributed that it is exposed to the total radiation (equal distribution over the entire surface), and taking the average path as 0.58 x radius. It has been shown by Lind,[45] however, that the combination proceeds under the experimental conditions just mentioned to within nearly 1% of complete combination. This was attributed to local condensation of the water so that it receives only a small part of the radiation it would receive if evenly condensed over the entire surface. The heterogeneous equilibrium in the presence of larger quantities of water would depend upon a great number of factors which make it difficult to calculate. The case has not been experimentally investigated. The case of the generation of high pressure in a sealed radium salt (§ 21), owing to the decomposition of residual water of crystallization, is interesting, because theoretically the equilibrium requires *low* instead of high pressure. It has been suggested by Lind (*loc. cit.*) that the gas is hydrogen alone, and that all the oxygen combines with the radium (or barium) salt.

[45] S. C. Lind, Trans. Amer. Electrochem. Soc., 34, 214 (1918).

39. Experiments of Wourtzel on the Decomposition of Gases.

The radiochemical researches of the Curie Laboratory were continued by Wourtzel [46] whose experimental method consisted in mixing purified emanation with the gas to be decomposed in spherical glass balloons of about 4 cm. diameter, enclosed over mercury but separated from it by a long capillary connection. The quantity of emanation employed was measured by the γ ray method. The ionization was calculated for complete absorption by an empirical formula $K = K_\infty (1 - C/Rp)$, in which K is the quantity of reaction produced by 1 curie of emanation at any pressure p, K_∞ is the amount of reaction at infinite pressure where the ionization and chemical action reach a maximum owing to complete absorption of the α radiation, R the radius and C a constant. The specific ionization for each gas was calculated from the results of Bragg,[47] Kleeman [48] and Taylor.[49] The amount of chemical action was determined by freezing the undecomposed gas and emanation in liquid air and measuring the decomposition products manometrically, and in some cases also chemically.

The decomposition of H_2S, NH_3, N_2O, and CO_2 was studied. The results are summarized in Table IX.

The effect of temperature on the reactions observed by Wourtzel is of great interest. The negative coefficient for H_2S, the positive one for NH_3, the minimum for N_2O at 18° have as yet remained unexplained. With respect to the M/N values reported by Wourtzel at temperatures other than ordinary, N refers to ionization at ordinary temperature, since no data were available at other temperatures. The failure of α rays to decompose CO_2 is further considered in § 50.

More recently Wourtzel [50] has elaborated a theory of chemical action by collision with the α particle, as distinguished from the ionization theory (see §§ 48-50). He employs his data on the decomposition of H_2S, NH_3, N_2O, and those of Scheuer (*loc. cit.*) for the combination of electrolytic gas to compare with the calculated number of encounters per second per curie of emana-

[46] E. E. Wourtzel, *Le Radium*, 11, 289-298; 332-347 (1919). *Journ. Russ. Phys. Chem. Soc. Proc.* 47, 210, 493-5 (1915). *Comp. rend.* 157, 929 (1913).
[47] W. H. Bragg, *Phil. Mag.* (6) 13, 333 (1907).
[48] R. D. Kleeman, *Proc. Roy. Soc.*, 79, 220 (1907).
[49] T. S. Taylor, *Phil. Mag.* (6) 21, 571 (1911).
[50] E. Wourtzel, *Journ. de Phys. et le Radium* (6) 1, 77-96 (1920).

TABLE IX

Decomposition of Gases by Emanation at Different Temperatures According to Wourtzel

Gas	*Temp.*	*Decomposed by 1 Curie Em.* c. c.	*M/N*	*% Energy Utilized*
H_2S	18°	1011	2.65	6.7
	95°	902	2.17	...
	220°	707	1.85	...
	—190°	Solid H_2S: Decomposition of same order as gas at 18°.		
NH_3	18°	282	0.80	1.2
	108°	556	1.58	...
	220°	824	2.33	...
	315°	900	2.55	...
N_2O	—78°	823	2.16	...
	18°	737	1.74	(4.0)
	220°	884	2.32	...
CO_2	18°	Very little decomposition observed.		

tion. The agreement with the measurements of chemical action is satisfactory, especially at higher temperatures. Wourtzel suggests that at the lower temperatures, where the number of encounters exceeds the number of molecules reacting, some of the encounters are not effective. In the case of N_2O, where at all temperatures the quantity of chemical action *exceeds* the number of encounters, Wourtzel assumes secondary action. This is the same assumption as proposed to explain excessive reaction by ionization, and it hardly appears possible with present data to decide between the two theories on statistical grounds. It also appears questionable if Wourtzel's assumption in calculating the number of encounters made by α particles that the dimensions of the particle are identical with those of the helium atom can be justified.

Chapter 8.

Kinetics of the Chemical Reactions Produced by Radium Emanation.

40. Classification of the Reactions.

In dealing with the kinetics of chemical reactions produced by radium emanation, two general factors must be considered: (1) change in the agent producing the reaction, namely, the radium emanation; (2) change in the system being acted on. The decay of emanation has been generally recognized as one of the controlling factors of the rate of reaction and has been taken into account by all authorities since Cameron and Ramsay first called attention to it. Besides the decay of emanation another factor controlling its effectiveness in producing chemical reaction is its distribution in the system being acted on. In a gaseous system, emanation is distributed as a gas and its effectiveness is limited only by the effective paths of the α particles in the gas phase, which subject has been treated in § 35. In a liquid system complete absorption of the α radiation occurs, provided the emanation is entirely confined within the liquid. If a gas phase exists, the distribution of the emanation between the two phases must be known as well as all the other factors involved in determining the proportion of radiation from the gas phase that will be effective on the liquid. In general, the reaction in the gas phase itself will be negligible compared with that in the liquid. In a liquid system the conditions of absorption of the radiation remain unchanged at maximum, unless a gas phase should be produced by the reaction. The inconveniences attending such a possibility can be avoided by the use of the α ray capillary as was done by Duane and Scheuer (§ 37).

In gaseous reactions a number of cases are to be considered. The simplest case is that of an elementary gas acted on in such a way that its volume and concentration remain constant while the product of reaction is continually removed from the field of

action. If its concentration (pressure) diminishes or increases at constant volume, then this change must be taken account of in regard to its influence upon the effectiveness of α ray absorption. Such a case would be represented by the ozonization of oxygen mixed with emanation at constant volume, where the ozone formed was being continuously absorbed by mercury. In a *mixture of gases*, a simple case is presented by electrolytic hydrogen and oxygen; the product water is condensed and nothing changes in the gas phase except the pressure. More complicated cases arise when the products of reaction remain in the gas phase, as in NH_3 decomposition. Not only does the question of reverse reaction then present itself, but also that of an indirect effect of the products in rendering the radiation effective for the primary reaction. Furthermore, in the case of mixtures one may inquire whether only one component is activated or more, and what the effect of a foreign gas will be in the mixture. These and other similar questions are natural ones from the kinetic standpoint. But before they can be attacked it is necessary to develop a general kinetic equation for the influence of emanation on gas systems as a function of the pressure, which is in turn itself a function of the rate of reaction, dependent upon the quantity of emanation, its rate of decay, the size of the vessel and other factors.

41. Development of General Kinetic Equation for the Action of Emanation When Mixed with Gases in Small Volumes.

The following equations were developed by Lind[1] from the standpoint of ionization, but the final general form, equation (3), is equally valid for the influence of emanation without any reference to ionization.

If N be the number of pairs of ions formed in a time interval t,

$$dN/dt = 3 \times 3.72.10^{10}.E_t.2.4.10^4.p.i.P/760. \qquad (1)$$

in which $3 \times 3.72.10^{10}$ is the number of α particles emitted per second by 1 curie of emanation in equilibrium with Ra A and C, E_t is the emanation in curies at any time, $2.4.10^4$ is the number of pairs of ions formed per cm. by each α particle along the

[1] S. C. Lind, *Journ. Phys. Chem.*, 16, 571; 591-4 (1912).

first two or three cms. of the path in air at atmospheric pressure, p is the average path in cms. as defined in § 35, i is the specific ionization for any gas compared with that of air under the same conditions, P/760 is the pressure reduced to standard conditions. Equation (1) may be condensed to the form: $dN/dt = kE_t.P = kE_0e^{-\lambda t}.P$, in which k is the ionization constant including all the constant terms of (1).

The relation between chemical action and ionization may be expressed as:

$$-dC/dt = \text{const.}\ dN/dt,$$

in which dC is the change in concentration of the substance undergoing reaction.

In the case where the rate of chemical action is measured manometrically by the decrease in pressure,

$$-dP/dt = \mu dN/dt, \qquad (2)$$

where $P = P_0 - \mu N$, if $P = P_0$ for $N = 0$. Combining equations (1) and (2):

$$-1/\mu.dP/dt = kE_0e^{-\lambda t}\ P, \text{ and } dP/P + k\mu E_0e^{-\lambda t}dt = 0$$

$$\log P/P_0 = k\mu/\lambda.E_0(e^{-\lambda t} - 1) \qquad (3)$$

$$P = P_0e^{(k\mu/\lambda)E_0(e^{-\lambda t} - 1)} \qquad (4)$$

Substituting to introduce N:

$$N = (1/\mu)P_0\ [1 - e^{k\mu/\lambda E_0(e^{-\lambda t} - 1)}\ ] \qquad (5)$$

For reactions being measured manometrically by the pressure change, equation *(3)* can be conveniently employed as a kinetic equation in the form:

$$k\mu/\lambda = \text{velocity const.} = \frac{\log P/P_0}{E_0(e^{-\lambda t} - 1)}$$

42. Application of Kinetic Equation to Experimental Results.

The kinetic equation developed in § 41 will be strictly applicable only in cases where all the constants included under k actually remain constant during the course of the experiment. This will be true for the specific ionization only when the products of reaction are removed from the field of action. As already pointed out this condition is satisfied by the electrolytic mixture of hydrogen and oxygen at ordinary temperature through the

condensation of water. For this reason the kinetic equation was applied by Lind (*loc. cit.*) to the results of Cameron and Ramsay for this reaction, as shown in Table X. It was also applied to some of the other reactions studied by them and by Usher. In the decomposition of CO and of NH_3 the partial pressures of the CO and NH_3 are used instead of the total pressures, including the decomposition products. The satisfactory constant in the case of CO indicates the correctness of such a procedure, and the absence of any influence of the CO_2 formed upon the rate of reaction, confirms Wourtzel's (§ 39) result that CO_2 is little acted on by emanation. On the other hand the results for the decomposition of NH_3 are in accord with the equation only for the first part of the reaction; during the latter part, where the products have accumulated, the apparent rate falls off owing to some

TABLE X

Application of Equation (3) § 41 *to the Results of Cameron and Ramsay and of Usher*

$2H_2 + O_2 = (2H_2O)$ (moist). Vol. = 2.186 c. c. $E_0 = 0.0465$ curie.			$2CO = CO_2 + (C)$. Vol. (calcd.) = 2.567 c. c. $E_0 = 0.025$ curie.		
t (days)	*P (mm.)*	$k\mu/\lambda$	*t (days)*	*P of CO (mm.)*	$k\mu/\lambda$
0.0	523.5	.....	0.0	297.0	——
1.02	487.0	(9.3)	0.81	282.0	17.2
2.07	442.0	(11.7)	1.89	263.0	17.9
3.07	405.6	12.9	2.8	251.0	17.8
4.13	384.5	12.7	3.8	245.0	16.1
4.99	369.5	12.8	4.8	233.0	17.3
6.11	352.2	12.8	5.8	225.0	17.5
7.07	343.5	12.6	6.8	221.6	17.0
9.11	321.4	13.0	10.1	218.0	15.2
10.16	319.3	12.7	14.8	206.2	16.0
11.04	316.6	12.5	19.9	208.4	(14.9)
12.10	312.3	12.5	23.8	201.4	15.1
97.0	291.0	12.6	26.8	200.2	16.2
	Mean	.. 12.71		Mean	.. 16.5

TABLE X—(*Continued*)

$2NH_3 = N_2 + 3H_2$ (Usher). Vol. = 2.406 c. c. E_0 = 0.145 curie.			$N_2 + 3H_2 = (2NH_3$?), Vol. = 2.30 c. c. E_0 = 0.1195 curie.		
t (days)	$v^{(2)}$ *(c. c.)*	$k\mu/\lambda$	*t (days)*	*P (total)*	$k\mu/\lambda$
0.0	0.909	...	0.0	745.6	....
0.07	0.895	8.3	0.79	720.8	(2.15)
0.76	0.781	8.2	1.76	714.1	(1.34)
1.08	0.735	8.3	2.77	707.6	(1.13)
1.75	0.664	8.0	3.77	701.6	1.04
2.08	0.630	8.1	4.85	694.3	1.03
2.78	0.581	7.9	5.77	690.1	1.01
3.75	0.527	7.7	6.76	686.6	0.98
4.75	0.493	7.4	7.76	683.1	0.98
6.75	0.441	7.1	9.76	677.1	0.97
7.75	0.431	6.8	11.0	675.0	0.97
8.75	0.421	6.7	12.8	672.4	0.96
13.77	0.399	6.2	14.8	671.9	0.98
32.0	0.385	5.9	17.9	669.1	0.94
	Mean	....		Mean	0.99

(2) The use of vol. instead of pr. in equation (3) is readily understood.

kind of reverse action, such as seen under the reaction: $N_2 + 3H_2$. Usher found little or no NH_3 formed, but the manometric effect would be in the same direction as that of a reverse action, even if it is only a mechanical loss of H_2.

A complete kinetic study of the reaction $2H_2 + O_2$ was more recently undertaken by Lind (*loc. cit.*) with the following objects: to study the applicability of equation (3) over wider variations of pressure, to enable the exact evaluation of M/N, to determine the influence of the size of the spherical vessel, and to establish the effect of varying the proportions of hydrogen and oxygen.

The apparatus used by Lind was a simplified form of that of Cameron and Ramsay and is shown in Fig. 6. The emanation was measured by the γ ray method after introduction into the emanation chamber. By comparison of the columns for per cent reaction (completed) and per cent emanation (decayed) it

TABLE XI

Application of Equation (3) to Results of Lind for Reaction $2H_2 + O_2 = (2H_2O)$ *in Glass Spheres of Different Sizes*

2 cm. Sphere. Vol. = 3.758 cm.³ Diam. = 1.925 cm. E_0 = 0.1464 curies.

5 cm. Sphere. Vol. = 61.321 cm.³ Diam. = 4.893 cm. E_0 = 0.1640 curies.

Days	*Hrs.*	*P(mm.)*	*% Reaction*	*% Em.*	*Const. kμ/λ*	*Days*	*Hrs.*	*P(mm.)*	*% Reaction*	*% Em.*	*Const. kμ/λ*
0	0.0	436.6	0.0	0.0	....	0	0	557.7	0.0	0.0	....
0	4.83	387.8	11.18	3.56	22.8	0	18.13	518.8	17.36	12.71	3.47
0	8.58	358.0	18.00	6.23	21.8	1	1.50	506.7	22.76	17.41	3.36
1	0.75	248.0	43.30	16.94	22.8	1	18.50	478.9	35.17	27.29	3.40
1	7.67	216.8	50.34	21.14	23.1	2	2.25	467.0	40.48	31.40	3.45
2	0.0	155.2	64.45	30.23	23.3	2	18.08	445.3	50.16	37.08	3.51
2	7.67	141.2	67.66	34.13	22.6	3	1.67	437.9	53.47	42.45	3.47
3	0.25	111.9	74.35	41.83	22.2	3	20.92	416.1	63.19	50.19	3.56
4	0.58	69.7	84.05	51.53	24.3	5	18.17	386.4	76.43	59.52	3.76
6	0.08	42.6	90.24	66.06	24.0	7	18.25	362.6	87.06	70.26	3.73
8	6:00	30.4	93.03	77.35	23.5	12	22.50	333.6	100.0	90.26	3.47
				Mean..	.23.04					Mean..	. 3.52

will be seen that the former runs far ahead of the latter, especially in the 2 cm. sphere where the reduction in pressure is greater. This shows that the agreement found by Cameron and Ramsay (§ 30) is the special case in which the relative pressure change is slight. In cases of large variation the pressure must be taken into account as has been done in equation (3). Complete justification of the treatment is seen in the agreement of the $k\mu/\lambda$ values over the whole range of the reaction.

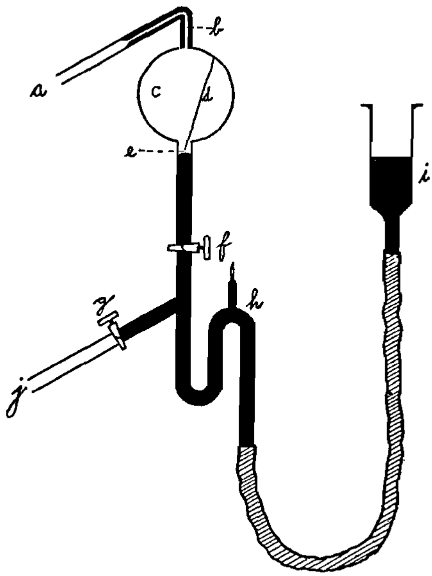

FIG. 6.

43. Influence of the Size of the Reaction Vessel, Law of the Inverse Square of the Diameter of the Sphere.

By determining the velocity constant of the interaction of electrolytic hydrogen and oxygen in several different spherical vessels of diameters from 1 to 5½ cms., Lind (*loc. cit.*) established a general relation, applicable up to a certain size. From the standpoint of the average path of the α particles in limited spherical volumes (§ 35), the nature of the relation can be predicted. Increase of diameter of the sphere lengthens the average path by the same ratio and therefore increases the quantity of chemical action in direct proportion to the increase of the diam-

eter. The pressure effect, however, of a given amount of chemical action will be *inversely* proportional to the volume and, therefore, to the cube of the diameter. Combination of these two oppositely directed influences predicts that the pressure change will be inversely proportional to the square of the diameter of the spherical reaction vessel, and therefore *velocity constants expressed in terms of pressure* (as in Equation (3)) *will diminish as the square of the diameter of the spherical reaction vessel increases.* By comparing the velocity constants $k\mu/\lambda$ for the 2 cm. and 5 cm. spheres in Table XI, it will be seen that a large decrease in the case of the latter was observed. In the following Table XII are summarized the results of Lind for spheres of several different diameters obtained by the same method.

TABLE XII

Effect on the Velocity Constant of the Reaction $2H_2 + O_2 = (2H_2O)$ *of Varying the Diameter of the Reaction Sphere*

Approx. Diam. of Sphere (cms.)	*True Diam. D (cms.)*	*Vol. of Sphere cm.*^{3}	$k\mu/\lambda$ *(found)*	$k\mu/\lambda \times D^2$
1	0.9647	0.4701	(89.6) [3]	83.4
2	1.925	3.738	23.04	85.3
3	2.924	13.272	9.92	84.8
4	3.963	32.58	5.30	83.2
5	4.893	61.32	3.52	84.3
5½	5.613	92.60	2.68	84.1
			Mean......	84.1

[3] Extrapolated value. See Chapter 11 on Recoil Atoms.

The results of Table XII appear to establish the nature of the law governing the influence of the size of the containing sphere on the velocity of the interaction of electrolytic gas as brought about by radium emanation intermixed with it. The fact that it is in agreement with the predictions of the principle of average path of the α particles supports the validity of the principle and its application in calculating ionization. On passing to volumes other than spherical, it has not been possible, as

stated in § 35, to give a mathematical treatment of the average path. One experiment was made with a cylinder 1.8 cm. in diameter and 4 cms. long of volume 6.787 c. c., equal to the volume of a sphere 2.375 cms. in diameter. Using 0.01219 curie of emanation, a value of $k\mu/\lambda$ was obtained of 14.8, which multiplied by $(2.375)^2$ gives 83.1, a value agreeing within the limits of experimental error with those of the spheres in Table XII. Results for more elongated cylinders are to be desired. The use of such a small quantity of emanation gave a pressure reduction of only 578.1 to 480.5 mm. in 30 days. Comparison of the rate of reaction and the rate of decay of emanation showed agreement within about 1%, thus confirming the experimental realization of Cameron and Ramsay's special case (§ 30).

It may be of interest to inquire how great the diameter of the reaction sphere may become before the validity of the relation $k\mu/\lambda = 84.1/D^2$ is impaired. Evidently it holds for the largest bulbs used in Table XII (5½ cms. diam.). By applying Equation (3) to the results of Scheuer for the same reaction (§ 38) a single value of $k\mu/\lambda$ may be found for still larger spheres. In his experiment with a sphere of 7.18 cms. diameter the pressure diminished from 1580 mm. to 1433.8 mm. in 26 days with 0.0613 curie of emanation, which gives a value of $k\mu/\lambda$ of *1.601*. The value calculated according to $k\mu/\lambda = 84.1/D^2$ is 1.633, showing that for a sphere of 7 cms. containing 2 atmospheres of electrolytic gas, the amount of reaction found is only 2% below the theoretical value for the completely utilized average path. On going up to Scheuer's sphere of 8.94 cms. diameter and a gas pressure of 1680 mm., $k\mu/\lambda$ (exptl.) is only *0.987* against 1.054 (theory). And in a sphere of 6 cms. diameter at the high pressure 11,445 mm., $k\mu/\lambda$ (exptl.) is only 0.3278 against 2.278 (theory). The difference is due to the number of α particles which can not complete their paths at this pressure before being completely absorbed. The limit of the applicability of the formula for average path appears to be about 7 cms. for a pressure of 1580 mm. of $2H_2 + O_2$, which would correspond to a diameter of 10 cms. at 1 atmosphere, corresponding to an average path in air of about 3.5 cms. One should expect that the general law of chemical action proportional to ionization by α particles would hold only over the first two or three cms. of path, where ioniza-

tion remains constant. This would doubtless be true for a single type of α particle, for example, from Ra C alone, but comparison with Bragg's ionization curves combined for all the α particles[4] shows that ionization per length of path for emanation in equilibrium would remain almost constant up to about 4 cms. from the source in air.

The interaction of hydrogen and oxygen mixed with radium emanation can come to an end through the approximate exhaustion either of the emanation or of the gaseous mixture being acted on; the latter takes place in small bulbs with high emanation, the former in large bulbs. The actual pressure (P) at any time t (or after decay of all emanation) may be calculated for any given case from the equation:

$$(\log P/P_0) / (E_0(e^{-\lambda t} - 1)) = 84.1/D^2$$

Contrary to the opinion expressed by some authorities, the ratio of quantity of emanation to quantity of reacting gas is not important from the kinetic standpoint. The ratio of emanation to reacting gases may rise continuously, as is the case in small volumes where the gases react at a faster percentage rate than the emanation decays, may pass through a maximum as in 3 cm. spheres with about 100 millicuries of emanation, or may fall continuously, as in larger spheres, without affecting the velocity constant. This shows that, while the ratio of emanation to gas influences greatly the actual velocity of reaction, it does not change the value of $k\mu/\lambda$, thus proving that the general kinetic equation proposed holds, regardless of the relative concentrations, except as provided for in the equation.

It may also be mentioned that the kinetic equation will hold in volumes even greater than those at which the average path formula no longer applies, but with very large volumes the pressure changes produced by attainable quantities of emanation would become too small for accurate measurement. There is also no reason to suppose that the same formula: velocity constant = const./D^2 should not hold for other reactions than $2H_2 + O_2$, with different values, however, for the constants involved.

[4] W. H. Bragg, "Studies in Radioactivity" (1912), p. 21; *Phil. Mag.* (6) 10, 323 (1905).

44. Use of Kinetic Results to Evaluate M/N.

The study of the reaction between hydrogen and oxygen provides through the general formula for spheres (preceding §) and the value of the average path of the α particle in spheres, a method of evaluating M/N which has great validity, since it depends not on any one experiment but on the results of a whole concordant series for which a general law has been demonstrated. It has just been shown that $k\mu/\lambda = 84.1/D^2$. Therefore for a sphere with $D = 1$, $k\mu/\lambda = 84.1$, and it is only necessary to evaluate k and solve for μ. λ is the decay constant for radium emanation $= 2.085 \times 10^{-6}$ sec.$^{-1}$. μ is an efficiency factor for the chemical effect of ions and may be expressed as $\mu = (M/N).(760/V.2.75 \times 10^{19})$. $K =$ ionization coefficient $=$ number of α particles per second for 1 curie of emanation in equilibrium with Ra A and C $(3 \times 3.72 \times 10^{10})$ x number of ions per α particle per 1 cm. of path (2.4×10^4) x specific ionization of the gas mixture (for $2H_2 + 1O_2$) $1/3\ (2 \times 0.24 + 1.09) = 0.523$) x average path for sphere of 1 cm. diam. (0.2967 cm.) x 1/760 (to refer to 1 mm. of pressure). Therefore, $k = 4.16 \times 10^{14}.1/760$.

Substituting in $k\mu/\lambda = 84.1$ and solving for M/N:

$M/N = \mathit{6.0}$, or $M_{H_2O}/N = 2/3\ M/N = \mathit{4.0}$. (See also end of this §.)

That is, for each pair of ions produced by emanation in the gaseous mixture $2H_2 + O_2$, *about 4 molecules of water are formed.* This is calculated on the basis that all the reduction in pressure represents the formation of water. If H_2O_2 is formed it must have but temporary existence, since in one experiment of Lind [5] an intitial pressure of 982.9 mm. of electrolytic gas was reduced in 12 days by 0.1868 curie of emanation at a volume of 3.375 c. c. to only 11.5 mm. The M/N value *4.0* is in fair agreement with that of Scheuer 3.7 (also see Kirkby, p. 125), but much higher than the older values of Cameron and Ramsay which were less than 1.0. The kinetic evidence of §§ 42 and 43 indicates that Cameron and Ramsay's low results are to be attributed to an incorrect report of the quantities of emanation used in their experiments, which were not the result of direct measurement *in loco* but of a calculation from the amount of radium in

[5] S. C. Lind, *Trans. Amer. Electrochem. Soc.* 34, 214 (1918).

the original solution. If the evolution or collection from the solution was inefficient, the quantities of emanation reaching the reaction chamber may well have been several fold lower than estimated. For example, the value of $k\mu/\lambda$ found in § 42 for one of Cameron and Ramsay's experiments was *12.71*, but, from the general formula for a vessel of that volume, should have been *32.43*.

In calculating the M/N value for the formation of water by the average path method, one assumption was made which requires some discussion. The average path was calculated assuming that all α particles of Ra A and C originate on the wall of the containing sphere, which involves the assumption that Ra A after being generated from emanation in the gas phase has time to diffuse to the wall before emitting its α radiation. No data having a very direct bearing on this subject appear to exist. A. Debierne[6] has made the most complete examination of the rate of diffusion of active deposit by using parallel plates at different distances apart exposed to emanation. His results show that the practical limits of diffusion are much smaller than the theoretical calculated from atomic weights, and indicate a particle 140 times as heavy as the atom of the decay products. Some direct experiments were undertaken by Lind (*loc. cit.*) by allowing the emanation to reach equilibrium in electrolytic gas in glass spheres of the same sizes as those used for the velocity of combination. By suddenly driving the gases before mercury into a new vessel, the initial γ radiation in the latter would disclose the quantity of Ra C transferred and consequently the proportion left on the wall of the reaction chamber. In a sphere of 2 cm. diameter filled with electrolytic gas at atmospheric pressure the percentage of Ra C transferred was 6.7%; or 93.3% was deposited on the original wall. From a 6 cm. sphere 11.6% passed into the new vessel; or 88.4% remained on the wall of the original. This result, not to be expected from Debierne's data, is probably due to heat convection. At any rate it is evident that under the experimental conditions a large part of the Ra C reaches the wall of even a 6 cm. sphere. This would not be necessarily true for Ra A in the same spheres owing to its much shorter life, but the velocity constants in Table XII do not in-

[6] A. Debierne, *Le Radium* 6, 97-108 (1909).

dicate any difference between large and small spheres for effectiveness of the emanation (plus decay products). Whatever assumption is made, therefore, as to position of decay products for one size must be made for all. The one made was that both Ra A and C completely diffuse to the wall before decaying. If one assumes instead that Ra A remains largely in the gas phase while Ra C diffuses to the wall, the value of the average path is changed from 0.5833 to 0.6667 times the radius, and the M/N value would be lowered to *3.50*. From considerations to be pointed out in § 48 a value slightly less than 4 has greater probability than one above 4. This discussion is deferred to § 48 where all the evidence for and against an ionic theory of the α ray effects is summarized.

Chapter 9.

Additional Relationships of the Radiochemical Effects.

45. Influence of Varying the Proportions of Hydrogen and Oxygen.

In studying the interaction of hydrogen and oxygen under the influence of radium emanation mixed with the gases, the effect of varying the relative proportions of the two components was investigated by Lind.[1] The effect of an excess of either gas on the rate of reaction can be predicted on the assumption that the change in rate will be in proportion to the ability of the mixture to absorb the energy of the α particle, which is in proportion to the ionization. The specific (molecular) ionization compared with air is according to Bragg (§ 13) 1.09 for oxygen and 0.24 for hydrogen. Consequently an initial excess of oxygen should increase the reaction velocity relative to that of the normal electrolytic mixture, while excess of hydrogen should produce the opposite effect. The velocity constant calculated from the general kinetic equation should be initially higher than the normal value in the case of excess of oxygen, and should continue to rise as the mixture becomes relatively richer in oxygen with the progress of the reaction. With initial excess of hydrogen exactly the opposite should be true; the velocity constant should be initially abnormally low and show a further fall as the mixture enriches relatively in hydrogen.

Both cases were experimentally investigated and the predictions just made were found to be fully confirmed, as will be seen from Table XIII. Since the specific ionization now becomes variable, the general kinetic equation is not strictly applicable. The development of a new equation taking into account the changing specific ionization or "stopping power" is so complicated that the simpler procedure has been adopted of using the

[1] S. C. Lind, *Journ. Amer. Chem. Soc.* 41, 542 (1919).

equation to show that the change in its velocity constant is proportional to the change in specific ionization. Since the velocity constant ($k\mu/\lambda$) now becomes a variable, it should be calculated over short intervals to avoid undue masking of its variability. To accomplish this the value of $k\mu/\lambda$ is calculated, not from the beginning through the entire time interval in each case, but from each measurement to the next, a procedure quite commonly employed in chemical kinetics.[2]

The equation may be written in this form:

$$\left(\frac{k\mu}{\lambda}\right)' = \frac{\log \frac{P_1}{P_2}}{E_o\,(e^{-\lambda t_1} - e^{-\lambda t_2})} \tag{6}$$

Table XIII gives the data for the initial mixture $4H_2$ to $1O_2$. In column 5 the application of equation (6) shows that $(k\mu/\lambda)'$ is not constant but falls approximately as required by the change in specific ionization (compare column 6). Column 6 is calculated from the normal value ($k\mu/\lambda = 84.1/D^2$) $= 10.65$ for a sphere of the size used, and from the change in specific ionization calculated by applying the simple law of mixtures to the values for pure hydrogen and oxygen.

A consideration of the results shown in Table XIII will throw light upon an important question, namely, whether it is only one component of the reaction, or both, which are activated by the α radiation; or, in terms of ionization, are both the hydrogen and oxygen ions capable of taking part in the chemical reaction produced at ordinary temperature? Since the rate of reaction appears to be proportional to the specific ionization of the *mixture*, this question is already answered in favor of the supposition that both ions are active. But a still more definite answer is obtained by calculating $(k\mu/\lambda)'$ for partial pressures of the components. In the last column of Table XIII are values of $(k\mu/\lambda)'$ calculated from the *partial pressure* of oxygen, and it is seen that the values rise, whereas the reaction is really slowing up from the rate shown by a normal mixture, which must be interpreted as meaning that the partial pressure of oxygen alone does not control the rate of reaction. The calculation from partial pressures of hydrogen would in this case not differ suf-

[2] J. W. Mellor, "Chemical Statics and Dynamics" (1904), pp. 31, 36, 37.

TABLE XIII

Effect of the Excess of H_2 on the Velocity Constant of the Reaction $2H_2 + O_2 = (2H_2O)$

Init. Mixt. $4H_2:1O_2$. Vol. = 11.64 c. c. Diam. = 2.812 cm. $E_0 = 0.1169$ curie.

Days	*Hrs.*	*Total Pr. mm. Hg.*	*Partial Pr. O_2*	*$(k\mu/\lambda)'$ (found)*	*$(k\mu/\lambda)'$ (calcd.)*	*$(k\mu/\lambda)'$ for Par. Pr. O_2*
0	0.0	682.8	136.6	....	....	.....
0	19.25	605.9	110.9	7.92	7.93	13.20
1	3.25	580.3	102.4	7.30	7.50	13.50
1	23.00	528.2	85.0	7.17	7.38	14.20
2	23.67	480.6	69.2	6.80	7.17	14.90
4	19.33	425.2	50.7	6.42	6.89	16.30
6	3.75	397.9	41.6	6.24	6.62	18.61
7	19.67	375.8	34.2	5.74	6.46	19.50
8	23.75	363.9	30.2	5.89	6.30	22.71
11	19.33	346.7	24.5	5.24	6.10	22.75
13	22.33	338.4	21.8	5.50	5.97	27.91
15	22.50	332.9	19.9	5.65	5.90	30.24

ficiently from that by the total pressures to make a decision, but may be undertaken for mixtures with initial excess of oxygen.

In Table XIV will be found data for mixtures with excess of oxygen.

In Table XIV the comparison with the theoretical values calculated from ionization is not made, since the change in specific ionization is not so great as in the case with the mixture $4H_2:1\ O_2$ (Table XIII), but it can be seen that the constants show a tendency to rise in all cases and begin abnormally high when compared with the normal value for electrolytic mixture, as required by theory.

From the data for the 2 to 1 and 4 to 1 mixtures in Table XIV it will be observed that when the hydrogen is exhausted, the pressure reduction does not stop entirely, but the velocity of reaction falls at once to one of an entirely lower order as indicated by the velocity constants in the last column. This is caused by some reaction that oxygen alone undergoes when acted

TABLE XIV

Effect of Excess of O_2 on the Velocity Constant of the Reaction $2H_2 + O_2 = (2H_2O)$

Orig. Mixt. 1 O_2:1 H_2. Vol. = 13.517 c. c. Diam. = 2.955 cm. E_0 = 0.1401 curies. Normal $k\mu/\lambda$ = *9.63.*					Orig. Mixt. 2O_2:1 H_2. Vol. = 13.849 c. c. Diam. = 2.983 cm. E_0 = 0.1542 curies. Normal $k\mu/\lambda$ = *9.45.*					Orig. Mixt. 4O_2:1 H_2. Vol. = 12.609 c. c. Diam. = 2.877 cm. E_0 = 0.1093 curies. Normal $k\mu/\lambda$ = *10.09.*				
Days	*Hrs.*	*Total Pr. mm. Hg.*	*Part. Pr. H_2 mm. Hg.*	*$(k\mu/\lambda)'$ (found)*	*Days*	*Hrs.*	*Total Pr. mm. Hg.*	*Part. Pr. H_2 mm. Hg.*	*$(k\mu/\lambda)'$ (found)*	*Days*	*Hrs.*	*Total Pr. mm. Hg.*	*Part. Pr. H_2 mm. Hg.*	*$(k\mu/\lambda)'$ (found)*
0	0.0	510.4	255.2	....	0	0.0	553.5	184.5	.....	0	0.0	660.3	132.1	.....
0	16.0	422.0	196.3	12.0	0	16.25	446.6	113.2	12.13	0	6.16	611.6	99.7	15.46
0	23.75	386.8	172.8	12.4	0	20.58	421.0	96.1	13.66	0	11.58	573.5	74.2	15.47
1	23.75	300.7	115.4	13.0	1	16.25	327.5	33.9	13.86	0	21.92	509.4	31.5	16.68
2	17.17	254.8	84.8	13.9	1	20.58	310.5	22.5	14.69	1	2.00	487.2	16.7	16.33
3	20.00	203.9	50.8	14.2	2	0.08	297.2	13.7	15.43	1	6.42	464.7	1.7	15.54
4	20.00	172.3	29.8	14.6	2	16.25	253.3	0.0	13.02	1	22.67	451.8	0.0	2.87
5	20.00	150.1	15.0	14.3	2	23.75	249.1	0.0	3.19	4	21.83	448.6	0.0	0.22
6	16.00	130.6	2.0	20.4	5	0.17	245.9	0.0	0.47	12	5.58	444.1	0.0	0.31
7	0.42	127.6	0.0	9.1	8	17.08	242.0	0.0	0.52	18	22.00	443.3	0.0	0.26

on by α rays, which is more fully discussed in the following section.

46. Action of α Rays on Pure Oxygen or Pure Hydrogen.

The limits of changing the proportions of hydrogen and oxygen, discussed in the foregoing section, are pure oxygen or pure hydrogen. According to the results of Lind (§ 33), under different experimental conditions, ozone is formed by the action of α rays on pure oxygen. In the presence of mercury a secondary reaction with the ozone formed might be expected, which is clearly indicated by the results near the end of the reactions in Table XIV. Scheuer (*loc. cit.*) found that emanation mixed with oxygen led to very little pressure reduction, but it was not stated whether the reaction took place in the presence of mercury. Direct experiments by Lind with the same form of apparatus as used for electrolytic gases (Fig. 6, p. 100) showed that a decided diminution in pressure does take place, but that the velocity of reaction is dependent upon the extent of the surface of mercury that is exposed. When the surface is only that exposed by the mercury ordinarily in the stem of the reaction bulb, the reaction is relatively slow; but, if the mercury is allowed to rise in the bulb and spread out, the rate of reaction increases many fold. This probably means that primary ozonization takes place in all cases, but that de-ozonization also takes place unless the opportunity for ready combination with mercury is presented. The surface of the mercury becomes black, loses its coherence, clings to the glass and is finally covered with a black powder, probably mercurous oxide. The repetition of this experiment under more definite conditions offers the possibility of an independent method of measuring ozone formation by α rays.

In the case of pure hydrogen mixed with emanation a similar but smaller diminution in pressure was observed by Lind (*loc. cit.*), accompanied by a darkening of the mercury and a loss of its coherence, though no powder became visible on the surface as in the case with oxygen. The diminution of pressure ceased after a time and could not be made to proceed further by increasing the mercury surface. To explain reduction of pressure in hydrogen exposed to α radiation, several possibilities present them-

selves. Usher[3] found in trying to cause hydrogen and nitrogen to unite under the action of emanation that the reduction in pressure was mainly due to some other action of the α particles, presumably a purely physical one. On the other hand Duane and Wendt[4] have discovered the existence of an active modification of hydrogen produced by radium emanation, which reacts chemically with sulfur at ordinary temperature to form H_2S which can be detected by passing over paper impregnated with a solution of lead acetate. Langmuir[5] has reported the discovery of a very active atomic form of hydrogen, and recently Wendt and Landauer[6] have described the activation of hydrogen by α rays and by the corona discharge, and present evidence of its triatomic nature. Though not so active as monatomic hydrogen, the triatomic form has been shown by Wendt and Landauer to react at ordinary temperature with sulfur, arsenic, phosphorus, mercury, nitrogen, and both neutral and acid $KMnO_4$. It is unstable and reverts to the ordinary form in about one minute. It can be distinguished from the monatomic form by the ease with which it passes through glass wool.

47. Comparison of the Chemical Effects of α and of Penetrating Rays.

Since the chemical reactions produced by α rays have been shown to be at least approximately proportional to the ionization in most cases, it is logical to inquire whether the same is true for the chemical effects of the penetrating rays. At any rate the question should be carefully investigated experimentally. There is quite a divergence of opinion on the subject. Besides the experimental difficulties, which are serious, some of the early attempts to explain β ray effects were directed toward a consideration of the primary charge carried by the β particles themselves, which are of course very insignificant in comparison with the large number of electrons liberated and positive ions produced by the passage of β particles through matter.

[3] F. L. Usher, *Journ. Chem. Soc. Lond.*, 97_I, 389 (1910).

[4] Wm. Duane and G. L. Wendt, *Phys. Rev.* (2) 10, 116-128 (1917).

[5] I. Langmuir, *Journ. Amer. Chem. Soc.* 34, 1310-25; 36, 1706 (1914); 37, 417 (1915).

[6] G. L. Wendt and R. S. Landauer, *Journ. Amer. Chem. Soc.* 42, 930-46 (1920).

The chemical effects of β and γ rays are so minute for nearly all *gas reactions* that a direct comparison of ionization and chemical action has not been possible in a strictly quantitative sense. Of course, by increasing the absolute quantity of the radioactive source this difficulty could in part be obviated, although this is hardly possible for γ radiation, the relative ionization produced by which is of the order of 1/10000 of that of the corresponding α radiation. But a still more serious difficulty is encountered in the low absorption coefficients of β, and particularly of γ rays, which precludes the possibility of anything approaching complete utilization of the radiation in a gaseous system of reasonable dimensions. For this reason the investigation of the chemical effects of penetrating rays has been mainly confined to liquid systems (§ 28), and then under such conditions that a very small proportion of the γ radiation is absorbed.

The most careful comparison of α and β-γ ray effects has been made by Usher.[7] Using emanation in a glass capillary tube of 0.17 mm. thickness, 0.208 cm.^{3} of electrolytic gas was produced by the action of the penetrating radiation from 0.067 mm.^{3} of emanation in one month, while the combined action of the α and penetrating radiation from 0.025 mm.^{3} of emanation till completely disintegrated gave a total of 5.840 cm.^{3} of electrolytic gas (including H_2 from some H_2O_2 formation). Reduced to the same quantities of emanation, the joint effect of the rays is seen to be about 75 times as great as that of the penetrating rays alone, or the effect of the latter is about 1.3% of the combined effect. This is about what one should expect from the relative ionizations or kinetic energies. This appears to be strong evidence in favor of the same relationship between ionization and chemical action as that which has been shown to exist for α rays.

It should be mentioned, however, that a different interpretation was put upon his results by Usher from that just proposed. By taking into account all the soft β rays which were not able to penetrate the thin glass wall, and by assuming that each one of them would have had the same power of decomposing water as those had which did penetrate the wall, Usher estimated that, where emanation is dissolved directly in water, and hence all

[7] F. L. Usher, *Jahrb. d. Radioakt u. Elektr.* 8, 323-34 (1911).

non-penetrating rays are absorbed, the proportion of decomposition by the α rays is not more than *twice* that produced by the β rays. Apparently Usher was led to this view through the assumption of chemical effect proportional to the primary charges of the β particles themselves, according to which all β particles would produce the same chemical effect, regardless of their velocity, kinetic energy, or penetrating power. This is not only contrary to the idea of equivalence of ionization and chemical action, since the charge carried by the β rays would fall many thousand fold short of accounting for the chemical effects in a sense consistent with Faraday's Law; but, in the case of the very soft β rays, the law of the conservation of energy would be contraverted, since they do not possess enough kinetic energy to account for the amount of water decomposition assumed by Usher. In other words, *the chemical activity of α or β rays must be attributed to their kinetic energy and ionizing power, not to their own charges, which in comparison with the secondary charges produced are wholly insignificant,* as would be shown by the fact that a single α particle from Ra C, having two positive elemental charges, produces in its total path in air about 237,000 pairs of positive and negative charges, and even more than this in some other gases. The total ionization for water by 1 α particle has not been directly measured, but is probably of the order 195,000 pairs of ions.

In § 36, Table VII, the results of Usher for the decomposition of water by emanation are seen to be considerably lower than those of Duane and Scheuer, using the α ray capillary method. Debierne[8] has measured the decomposition of water by the penetrating rays from a radium salt, and found that 0.115 cm.^{3} of electrolytic gas are formed per day per gram of radium. This rate of decomposition is somewhat lower than that found by Usher per curie of emanation, as would be expected, owing to the greater absorption of radiation in Debierne's apparatus by the double glass wall and by the salt itself.

48. General Discussion of Ionic-Chemical Equivalence.

All the experimental evidence bearing on this subject has been presented in the foregoing sections except that pertaining to

[8] A. Debierne, *Comp. rend.* 148, 703-5 (1909).

recoil atoms which will be treated in Chapter XI. A general summary of the results is not without interest, although it may be impossible to reach a final conclusion acceptable to all authorities, from the data at present available.

It has been shown that in nearly all the reactions brought about by α rays that have been investigated there is an approximate statistical agreement between the number of ions generated and the number of molecules acted on. This appears to be true to the same degree of approximation both in gaseous and liquid systems. The results have been brought together for comparison in Table VII, § 36. It will be seen that the M/N ratio varies in different reactions from about 0.5 to about 4.0. An agreement within these limits for such a variety of reactions proceeding both with and opposed to the chemical free energy in both liquid and gaseous systems, when the disagreement might have been many million fold in either direction, appears to have fundamental significance and to warrant the application of a modified form of Faraday's Law to these reactions.[9]

Besides the direct evidence from α particles, it was shown in § 45 that when the proportions of hydrogen and oxygen are varied, the reaction to form water changes its rate in a ratio that can be predicted from the change in specific ionization of the mixture. Passing to other forms of radiant energy which produce ionization accompanied by chemical action, it was shown in § 47 that the same equivalence holds in the decomposition of water by β radiation. In § 33 the results of Krueger for the ozonization of oxygen by Lenard rays (high velocity electrons) were cited to show that the same relation exists; finally, in Chapter XI it will be shown that the recoil atoms from α radiation cause the combination of H_2 and O_2 in the same proportion to the ionization as found for α particles. Such evidence has been sufficient to convince many authorities that ionization is directly involved in the production of chemical reaction. On the other hand the results of Scheuer on the formation of water (§ 38) and those of Wourtzel (§ 39) on the decomposition of H_2S and of N_2O, which show M/N values exceeding unity by two to four fold, have convinced Debierne, Scheuer, and Wourtzel that

[9] S. C. Lind, *Trans. Amer. Electrochem. Soc.* 21, 177-84 (1911); *Journ. Phys. Chem.*, 16, 564-613; *Le Radium*, 9, 426-31; *Zeit. phys. Chem.*, 84, 759-61 (1913).

the ions are not the intermediate products causing the chemical action. Debierne[10] has proposed a theory of *thermal decomposition* along the path of the α ray but extending outside the limits of ionization and therefore statistically exceeding the ionization. Wourtzel (*loc. cit.*) finds in the negative temperature coefficients, which he obtained for the decomposition of H_2S and of N_2O, grounds for rejecting the thermal theory of Debierne and has substituted a theory of collision.

As already stated, the writer is of the opinion that the statistical agreement between ionization and chemical action, although inexact, points strongly to the intermediation of ions in bringing about the chemical reactions. The departures from the direct requirements of electrical and chemical equivalence are not too great to be brought into accord by making possible assumptions in regard to the mechanisms of reaction, which assumptions are quite within reason, although it is impossible with present data either to prove or disprove them absolutely. At any rate the departures of M/N from unity are quite small when compared with the real exceptions to be taken up in the following section. It might also be mentioned that whether ionization is primarily involved in the chemical reactions brought about by radiation, or whether it is a secondary accompaniment, it is at the present time the most convenient index of reference and can readily be made a means of comparing chemical action with any factors involved in the absorption of the energy of radiation.

Before going on to a consideration of the large exceptions from the general rule of equivalence of ionization to chemical action, the case of the combination of electrolytic hydrogen and oxygen under the influence of α rays will be used as an example to illustrate the possibility of proposing a mechanism of reaction that will explain the value $M_{H_2O}/N = 4$, without violating the general principle of equivalence.

Millikan, Gottschalk and Kelly (*loc. cit.*) have shown that the ionization of a number of ordinary gases by α particles consists exclusively in the removal of a single electron from each molecule affected, thus leaving an equal number of singly positively charged gaseous ions, which in the case under consideration would be H_2^+ or O_2^+. Of course there will be a certain tendency for immediate recombination of the electrons with the

[10] A. Debierne, *Ann. de Physique* (9) 2, 97-127 (1914).

oppositely charged ions but our general knowledge of the recombination of gaseous ions[11] informs us that its rate is not exceedingly great, and on account of the large excess of electrically neutral H_2 and O_2 molecules in the gaseous mixture, there will be ample opportunity for the free electrons to attach themselves to these molecules, forming negative ions H_2^- or O_2^-. The chemical activity of ions may be admitted on general grounds, and it is therefore fair to assume that all four kinds of ions can form H_2O_2 by combining with the hydrogen or oxygen present. If it is then assumed that each molecule of H_2O_2 retains its positive or negative charge until it is reduced by electrically neutral hydrogen to form two molecules of water from each molecule of H_2O_2, we should thus have as a net result from each original pair of ions two molecules of charged H_2O_2, each of which would produce by combination with H_2 two molecules of H_2O, making *four* molecules of H_2O for each original pair of ions. It has already been shown that Scheuer found 3.7, and that the results of Lind give a value either slightly less (3.5) or exactly four, depending upon what assumption is made as to the position of Ra A in the reaction vessel at the time of its decay. A value somewhat below 4 could be explained by cross reactions between charged molecules; for example, it could be assumed that the H_2O_2, actually found as a product of the reaction by Scheuer, had resulted from its stabilization by becoming electrically neutralized, preventing its reduction by hydrogen. The mechanism just proposed at least shows that the ratio $M/N = 4$ is still within the limits of possible ionic explanation without resorting to other theories. If it be assumed with Bodenstein (§ 55) that a free electron can attach itself to activate a molecule, is again detached at the moment of reaction, and continues to act thus through a large number of cycles until consumed by some reaction in which it is not again liberated, there is almost no limit to the multiple activity of a single electron.

49. Exceptions to Ionic-Chemical Equivalence—Reactions in Which M Exceeds N.

By consulting the column of M/N values given in Table VII, § 36, in which M is the number of molecules involved in a given

[11] J. S. Townsend, *Phil. Trans. Roy. Soc.* 193A, 157 (1899). R. K. McClung, *Phil. Mag.* (6) 3, 283 (1902); P. Langevin, *Thesis Paris* (1902), p. 151.

chemical reaction and N is the number of ions produced by the radiation, it will be observed that the cases in which M exceeds N fall into two general classes, those in which the M/N ratio lies between 1 and 4, and those in which it attains values of an entirely different order amounting to several thousand. With respect to those values falling in the former class it has been suggested in the foregoing paragraph that they do not constitute real exceptions, but that by making certain assumptions as to the mechanism of the reactions, an agreement between ionization and chemical action in a sense concordant with Faraday's Law may still be attained. In the case of the reaction brought about between hydrogen and oxygen by α rays, such a mechanism was proposed and discussed in detail in § 48. On account of our incomplete knowledge of the entire behavior of gaseous ions, and also on account of an insufficiency of exact experimental data, it does not appear possible at present to reach a final decision as to the exact relation between gaseous ionization and chemical action, nor would it be profitable to discuss theoretical possibilities as to exact mechanisms for other reactions. The number of possible variables exceeds greatly the number of equations now available for the solution of the problem.

Of the second class of reactions, in which M exceeds N by a large quantity, there is at the present time only one example, namely, the interaction between hydrogen and chlorine gases. This particular reaction has also been of great *photochemical* interest for more than a generation. The classical experiments of Bunsen and Roscoe[12] followed the work of Draper[13] in calling attention to the importance of this most prominent example of photochemical action, and further investigation of the various phases of the reaction has continued to the present time. It has been repeatedly shown that the activity of the hydrogen-chlorine mixture with respect to light varies with the purity of the mixture. The influence of the impurities exhibits itself in retarding the rate of the photochemical action and of lengthening the duration of the so-called "induction period" during which the rate of

[12] R. Bunsen and H. E. Roscoe, *Ostwald's Klassiker Nos. 34 and 38* (Leipzig, 1892). Orig. Refs. *Pogg. Ann.* 100, 43-88; 481-516; 101, 235-63 (1857); *ibid.*, 108, 193-273 (1859).

[13] Draper, *Phil. Mag.* (3) 23, 401 (1843).

reaction increases to a maximum. Chapman and MacMahon[14] have made exhaustive investigations of the *inhibition* of the photochemical interaction of hydrogen and chlorine. They have determined that *oxygen* is one of the most effective inhibitors and that the rate of reaction is inversely proportional to the quantity of oxygen present for oxygen contents from 0.08–1.0% by volume. They later showed that ozone is a very effective inhibitor. These discoveries have a very important bearing on the theory advanced to explain the excessive action of α rays on the $H_2 — Cl_2$ mixture.

As has already been stated (p. 85), the results of Jorissen and Ringer on the combination of $H_2 + Cl_2$ under the influence of penetrating rays enabled Lind to estimate that the M/N ratio exceeded unity by 100 to 1000 fold. This exceptional ratio led Bodenstein and Taylor (*loc. cit.*) to determine the effect of α rays on the same reaction. It was found that the reactivity of the mixture varied with its purity, as in the case of the photoreaction, and that in a mixture of maximum sensitiveness at least 4000 molecules of H_2 and Cl_2 combine for one pair of ions formed. As will be shown in the following chapter, Bodenstein calculated that the rate of the photochemical interaction of H_2 and Cl_2 exceeds the predictions of *Einstein's photochemical equivalence law* by a factor of about 10^6. Bodenstein was led to propose an electronic theory for photochemical action according to which an electron primarily liberated by any form of radiation can successively activate a large number of chlorine molecules, which then react with hydrogen, again liberating the electron at the time of reaction. This process would continue indefinitely from even a small number of initial free electrons except for the fact that finally the electron activates a foreign molecule (Chapman's inhibitors) and is not again liberated by the reaction. Bodenstein assumed oxygen to be the inhibitor in this case and that the ozone formed again decomposes to give oxygen. This fits with a number of other observations, namely, the inhibitive effect of oxygen and of ozone actually observed by Chapman and MacMahon, and with the observation of Lind that ozone formation is statistically equivalent to the ionization, from which it follows that the free electrons are consumed in the reaction. It also explains why the reaction does not proceed after

[14] D. L. Chapman and P. S. MacMahon, *Journ. Chem. Soc. Lond.* 95_I, 959-64; 95_{II}, 1717-20 (1909); 97_I, 845-51 (1910).

cessation of the radiation. As will be seen later, Bodenstein had to abandon the theory as applied to photochemical action of chlorine gas on account of the lack of ionization which he had assumed; but in the case of the action as produced by α particles where we have actual ionization, his theory remains applicable, in principle at least, to explain the abnormally high value of the M/N ratio. As alternative theories we shall have that of Nernst for the photochemical interaction $H_2 + Cl_2$ and the later one of Bodenstein, both of which will be presented in the following chapter. The fact that the $H_2 + Br_2$ mixture at ordinary temperature is not photo-sensitive and that its M/N value for α radiation is normal is of much interest.

50. Exceptions to Ionic-Chemical Equivalence. Reactions in Which N Exceeds M.

A study of the M/N ratios for various reactions in Table VII, § 36, shows that the cases in which the ratio drops below unity may be divided into those where the departure from unity is not below 0.5, and those where considerably lower values are attained. The case of slight departures needs no further discussion; the agreement may be regarded as satisfactory from the data at present available. The small deviations might be explained either on ionic grounds or by the assumption of some recombination to form the original product, thus reducing the reaction efficiency.

The cases in which the M/N ratio drops to much lower values seem to divide themselves into two classes, those where difference in state of aggregation is the controlling factor, and those in which the inherent properties of the reaction itself produce the low rate.

In the case of the decomposition of water it is very evident that the state of aggregation plays a large rôle. It has been shown in § 37 from the results of Duane and Scheuer that, while water in the liquid state is readily decomposed by α radiation in almost exactly the quantity required by ionic-chemical equivalence (or by electrolysis), the decomposition of ice under the same conditions is only about 5% of that of water. While for water vapor for the same amount of α radiation absorbed, the decomposition showed variable values somewhat

lower yet than those for ice. On the other hand Wourtzel (§ 39) found that the decomposition of solid H_2S at $-190°$ was of the same order as found for the gas at 18°. This does not necessarily mean that the decomposition of gaseous and solid H_2S at the same temperature would be equal, since Wourtzel found the rate of decomposition of the gas at higher temperatures to have a marked negative temperature coefficient, which, if continued to lower temperatures, might mean that the decomposition of the gas at $-190°$ would be (were it possible to determine it at this temperature) much higher than at 18°. It is difficult to find a plausible explanation for the results for water vapor and ice. In the case of water vapor one would be inclined to attribute the low value to recombination owing to the greater mobility of the system, but one is confronted with the case of ice, where mobility must be at a minimum, and yet the decomposition is much lower than that of water. The explanation might be entirely through temperature effect. This would require a maximum at ordinary temperature for the rate of decomposition of water. While Wourtzel has observed a minimum for N_2O at ordinary temperature, no maxima have yet been found. Since the temperature coefficients themselves remain unexplained, speculation in this direction is not illuminating.

To return to a consideration of gases, Wourtzel found in the case of CO_2 but slight decomposition, which he attributed to the greater stability of this compound, in other words, to the excessive amount of energy necessary to bring about its decomposition. Such a view is not in accord with the ionization theory of the reactions, since we know that CO_2 is readily ionized by α particles and that the amount of energy expended in producing its ionization is greatly in excess of that necessary for its chemical decomposition. As will be seen in the following section, there does appear to be some tendency for reactions proceeding in the direction of the chemical free energy to utilize a greater proportion of the kinetic energy of α radiation than do those taking place opposed to the free energy. But among those of the latter class there is no distinct tendency for the reaction to be controlled by this factor, and it is very certain that the failure of the decomposition of CO_2 gas by α rays is not due to lack of the necessary kinetic energy or of ability of CO_2 to absorb it, as evidenced by the ionization.

The question of the chemical action of α rays on solids has not been very thoroughly examined experimentally. As pointed out in §§ 28 and 36, the decomposition of some of the halides of the alkalis and alkaline earths has been investigated with penetrating radiation and found to be very small, in some cases almost zero. It is very fortunate that all solid substances are not attacked and chemically changed by radium radiations, as it would be impossible to carry out manometric measurements in glass or other vessels or to determine the true volume of radium emanation, if gases like oxygen, for example, were being continually liberated from the glass wall. There is no evidence of such being the case. Radium emanation may be retained in glass without the production of measurable quantities of pressure. It is very desirable to extend the investigation of the chemical effects of α rays to other solid substances both crystalline and colloidal.

It is interesting to point out that no great deviations have yet been observed of the M/N value for reactions of any substances in the liquid state, that the deviations in the solid state are all in the direction of low values of M/N, while in the gaseous state we have examples of large deviations from unity in both directions.

51. Energy Utilization of α Rays in Chemical Reactions.

In the last column of Table VII, § 36, are estimates of the percentage of the total energy of the α rays absorbed in a given system which is utilized by the resulting chemical action. The values have direct significance only in the cases where the reaction produced is opposed to the chemical free energy and therefore requires the expenditure of external energy. Values are also given, however, for the reactions proceeding with the chemical energy, in order to show that with the one large exception of the hydrogen-chlorine reaction, and to a much less degree that of hydrogen-oxygen combination, the order of the values is not very different from those of reactions opposed to the chemical free energy. This indicates that the chemical free energy does not, at ordinary temperature, play an important part in reactions produced by α particles. In other words, it appears necessary to do work on the molecules to render them chemically active,

and from the low energy utilization, it is evident that the work of the primary action involves energy quantities very much in excess of the net chemical energy, and that the amount of energy necessary to do this work is of the same order, whether the reaction is proceeding with or opposed to the chemical energy. If ionization is the intermediate step involved, this is just what would be expected. Since the energy necessary to form a pair of ions ($5.5.10^{-11}$ ergs) is large compared with the chemical energy of reaction referred to a single molecule, the energy transformation will be small. For example, if the M/N value is unity for a reaction of which Q = 100 Cals., q or the heat of reaction referred to a single molecule would be 6.10^{-12} ergs, and the energy utilization would be about 10%.

For most of the reactions where expense of energy is actually required the utilization factor is about 2% or less. Warburg[15] has pointed out that a low order of energy transformation is one of the chief characteristics of *photochemical* action. Warburg explains this by the assumption of a primary reaction consisting in splitting the molecules into atoms, a process that would require much more energy than that involved in the finally resulting chemical reaction, were it wholly molecular in mechanism. It does not appear at all impossible that free atoms are the intermediate products in photochemical reactions, while free ions and electrons may be the intermediate products or agents in reactions produced under ionizing conditions.

It might be mentioned that the values for energy transformation given in the last column of Table VII vary considerably in reliability. The later values for water formation, and for decomposition of water, ammonia, hydrogen sulfide, and nitrogen protoxide may be accepted with assurance. The data involved in most of the other cases are older and perhaps should be verified before they can be accepted with the same degree of certainty.

52. Chemical Action Produced by Electrical Discharge in Gases.

The subject of the chemical effects of electrical discharge through gases is too large to be considered in its entirety within the limits of the present work. Attention will be confined to

[15] E. Warburg, *Sitzb. Akad. Wiss. Berlin*, pp. 746-64 (1911).

those phases of the subject which are more closely related to radiochemistry and to the ionic theory of gas reactions.

As soon as it had been shown that ozone formation from oxygen is proportional to, and probably statistically equal to, the ionization (§ 33) both in the cases of α radiation and certain kinds of electronic discharge, the application of the same principle to the broader field of ozone formation by silent, spark, and other forms of electrical discharge, followed naturally. Theories were independently proposed by Kabakjian,[16] by Lind,[17] and by Krüger[18] which were practically identical. The generalization was made that probably in all cases ozone formation in gaseous oxygen is the result of the primary ionization of oxygen by some form of electronic discharge. The quantity of ionization involved in the ozone formation is not directly related to the flow of current, but is the far greater number of ions produced in the gas by electronic shock (§ 16), which never reach the electrodes and therefore take no part in the electrical conduction, since the intensity of ionization far exceeds the limiting conditions for attaining saturation current. This predicts that the quantity of ozone formed should not be related to the current flowing, as required by direct application of Faraday's Law, but should be a much greater quantity. The experiments of Warburg[19] on ozone formation by silent discharge confirm this fully. Under some conditions Warburg found that about one thousand fold as much ozone is formed as would correspond to the current, or that instead of the theoretical 96,500 coulombs required per chemical equivalent, less than 100 coulombs suffice for the production of one gram-equivalent of ozone. Hitherto it has not been possible to confirm the theory that the total ozone formation would be accounted for by the ionization by electronic shock, because we have no means of measuring the total ionization produced. Conversely the conditions under which ionization by shock have been measured[20] are not suitable for the formation and measurement of ozone.

Recently the subject of ozone formation in corona discharge

[16] D. H. Kabakjian, *Phys. Rev.*, 31, 122-35 (1910).

[17] S. C. Lind, *Trans. Amer. Electrochem. Soc.*, 21, 181-3 (1912)

[18] F. Krüger, *Phys. Zeit.*, 13, 1040-3 (1912).

[19] E. Warburg, *Sitzb. Akad. Wiss. Berlin*, p. 1011 (1903) ; *ibid.*, p. 1228 (1904). *Ann. d. Physik* 20, 734-42 (1906) ; *ibid.*, 20, 751 *et seq.* (1906).

[20] See the discussion of Townsend's work in Chapter 4.

has been investigated by Anderegg [21] and by Rideal and Kunz.[22] Anderegg expresses the opinion that oxygen atoms are probably present in all cases of ozone formation, but defers judgment as to whether ozone is formed from oxygen ions. Rideal and Kunz have paid especial attention to the distribution of ozone in the direct current corona of positive or negative sign. Their measurements of the quantity of ozone were made by two independent methods, chemical and photometrical. While the quantities of ozone formed in the positive and in the negative corona are approximately the same, the distribution differs in a marked manner in the two cases. The various ways in which ozone can be formed in the light of the radiation hypothesis (see following chapter) were also reviewed by Rideal and Kunz, and the conclusion drawn that molecules of one kind can be activated by radiation to different extents.

The combination of electrolytic hydrogen and oxygen under the influence of electrical discharge has been investigated by Kirkby.[23] The experimental conditions were regulated so as to parallel those employed by Townsend (§§ 16 and 18) in his studies of ionization by collision. Very low gas pressures (a few mms. of Hg) were used. The distance between the electrodes was varied from about 0.25 to nearly 2 cms. Kirkby found that the rate of combination is proportional to the current passing, and that about 4 molecules of H_2O are formed per pair of ions. It is very interesting to observe that this number is the same as that obtained by Lind (and practically the same as that of Scheuer) (*loc. cit.* § 48) for the same reaction under the influence of α particles. Kirkby concluded that hydrogen molecules react with uncharged oxygen atoms, which are dissociated by collision with electrons under certain conditions. Only one half of the collisions of electrons with the necessary velocity actually results in the dissociation of the oxygen molecule. For the action within the positive column Kirkby proposed a general formula: $N_{H_2O} = 7.9p.e^{-42.7p/Y}$, in which p is the pressure in mms. and Y is volts.cm^{-1}. The applicability of the formula is independent of the apparatus.

[21] F. O. Anderegg, *Journ. Amer. Chem. Soc.* 39, 2581-95 (1917).
[22] E. K. Rideal and J. Kunz, *Journ. Phys. Chem.* 24, 379-93 (1920).
[23] P. J. Kirkby, *Phil. Mag.* (6) 7, 223-32 (1904); 9, 171-85 (1905); 13, 289-312 (1907); *Proc. Roy. Soc.* 85A, 151-74 (1911).

Among other gas reactions produced by electrical discharge may be mentioned the very careful investigation by Davies[24] in LeBlanc's laboratory at Leipzig of the decomposition and formation of ammonia in a Siemens tube. Davies investigated the reaction and equilibrium from the standpoint of the application of the mass action law. He found that the course of the reaction may be expressed by a first order equation, that the rate of decomposition is approximately proportional to the current strength, and that the rate of decomposition has a very small temperature coefficient, the rate at 100° being double that at ordinary temperature. Excess of hydrogen was found to lower the rate of decomposition, while excess of nitrogen increased it. Equilibrium attainable from both directions was almost independent of the current strength and corresponded to ammonia formation to the extent of 6% of the maximum possible. With excess of either component the equilibrium changes in favor of further ammonia decomposition. The law of mass action is not applicable to the equilibrium. The rate of ammonia formation decreases slightly in excess of nitrogen and increases slightly in excess of hydrogen; this result is in accord with those for influence of excess on the decomposition, but are not those that would be expected by analogy with influence of excess of components in water formation by α rays (§ 45), where the excess of lighter gas diminished the rate while excess of the heavier increased it. Falckenberg[25] and Pohl[26] have studied the decomposition of ammonia in a Siemens tube rather from the physical and electrical standpoint and find Faraday's law inapplicable to the relation between current flowing and quantity of ammonia decomposed. From what has been said previously in regard to ozone formation it is evident that one should not expect any direct relation between the two. To make the statement more general it is quite as unreasonable to expect equivalence between the current flowing and the chemical effect in the case of electrical discharge through gases, as it would be to expect equivalence between the total primary charge of α rays and their chemical effects. In both cases equivalence must be sought in the far greater number of ions produced by collision.

[24] J. H. Davies, *Zeit. phys. Chem.* 64, 657-85 (1908). M. LeBlanc, *Verh. Sächs. Ges. Wiss.*, Leipzig, 66, 38-63 (1914).
[25] Falckenberg, *Thesis*, Berlin (1906).
[26] R. Pohl, *Ann. d. Physik* (4) 21, 879 (1906).

Further consideration of the experimental data on the chemical effects of the passage of electrical discharge through gases is not within the scope of this work.[27] In its most general aspects the subject may be regarded as having great scientific and perhaps important commercial possibilities which are well worthy of further research. For example, the possibility of an electrochemical process in which only 100 coulombs are required for the production of one chemical equivalent ought to prove attractive to the electrochemical engineer, provided the energy relations should not prove to be too unfavorable.

Besides the reactions produced by electrical discharge in gases at ordinary pressure there is a class of reactions observed at low pressures which may or may not be of chemical nature. The "clean up" of gases in spectrum tubes has been observed for many gases, but is especially puzzling for the gases of the inert series where we can not assume ordinary chemical reactions to take place. Although a mechanical or electrical explanation, such as that discussed for the hardening of X ray tubes (§§ 16 and 18) might be proposed, Collie[28] has recently observed the clean up of pure xenon in a manner very puzzling to explain. Xenon differs from the other inert gases in that heating does not again liberate it from the electrode or "splashed" mirror surrounding the electrode. Using platinum, aluminum and copper electrodes, Collie cleaned up more than 2 c. c. of xenon, of which he was unable to recover more than a few per cent even by chemically dissolving the electrodes, the mirror and the glass spectrum tube itself. Collie was almost forced to conclude that xenon had entered into some form of chemical combination from which it was not liberated as gas by the radical treatment employed. Radium emanation has been found by several authorities[29] to be cleaned up in a spectrum tube in a similar way. Since radium emanation can always be detected by its γ radiation it would be very interesting to repeat the experiments of Collie employing emanation instead of xenon to ascertain if any light would be thrown upon the nature of the "clean up."

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[27] References to the literature will be found in the paper of Davies (*loc. cit.*).

[28] J. N. Collie, *Proc. Roy. Soc.* 97A, 349-54 (1920).

[29] Rutherford, "Radioactive Substances" (1913), p. 482.

don recently presented[30] the results of an investigation of the disappearance of gas in the electric discharge, from which it appears that the phenomenon is closely connected with the appearance of a glow in the discharge tube, which is believed to result from a reversible chemical action.

53. Production of Free Electrical Charges by Chemical Action.

Related to the question of the production of chemical action by ionization is the converse one as to the liberation of charges by chemical reaction. Various opinions have been expressed as to the reality of this phenomenon. There can be no question but that chemical action is often accompanied by the liberation of electrical charges, but whether or not this is ever true in a homogeneous gaseous system where there is no possibility of the accompanying influence of high temperature or of some physical process, requires careful consideration.

By introducing a gold leaf electroscope directly into a mixture of hydrogen and chlorine gases and causing them to react under the stimulation of light, J. J. Thomson[31] showed most conclusively that no free charges are produced either in the "induction period" or during vigorous reaction. X rays projected into the same system caused the gold leaf to discharge, proving its sensitiveness, but failed to increase the rate of combination of hydrogen and chlorine as observed by the Bunsen and Roscoe actinometer. It might be mentioned parenthetically that this does not prove that X rays do not cause hydrogen and chlorine to react (proportionately to the ionization), since the sensitiveness of the gold leaf discharge to detect ions and that of the Bunsen and Roscoe actinometer to detect the disappearance of molecules by diminution in volume are of a wholly different order. Kümmell[32] later thought he had found evidence contrary to that of Thomson, but Thomson's result was confirmed by a very careful investigation by LeBlanc and Vollmer,[33]

[30] *Phil. Mag.* (6) 40, 585-611 (1920). (Conducted by N. R. Campbell and J. W. H. Ryde.)

[31] J. J. Thomson, *Proc. Camb. Phil. Soc.*, 11, 90 (1901) ; "Conduction of Elect. Through Gases," 2nd Edit., p. 229.

[32] G. Kümmell, *Zeit. Elektrochem.* 17, 409 (1911).

[33] M. LeBlanc and M. Vollmer, *ibid.*, 20, 494-7 (1914).

who also demonstrated for the first time a chemical effect of X rays in a gas reaction ($H_2 + Cl_2$).

On the other hand Haber and Just[34] have demonstrated in an extended series of experiments that the action of certain gases, including water vapor, the halides and phosgene, on alloys or amalgams of the alkali metals results in charging the metal positive owing to the liberation of electrons from its surface. Haber and Just demonstrated that temperature has an influence; iodine vapor at $-79°$ C. had no effect, while at $+3°$ there was an effect which became strong at $+13°$. They showed that the combined effect of light and chemical action emits more electrons than the sum of the separate emissions. Other metals than the alkalis show an effect if the temperature be raised. Aluminium begins to show an effect at 180°, which becomes rapid at 240°. The unipolarity of the effect begins to disappear at higher temperatures. Amalgams of Cs, K, and Li gave negative *ions* instead of electrons. The quantities of electricity emitted were far below Faraday equivalence; for example, the formation of one gram-molecule of KCl was associated with an emission corresponding to 65 coulombs instead of 96,500.

In a study of the oxidation of metallic Na, K and alkaline earths, Reboul[35] showed that the electrical effects accompanying these reactions are weak and difficult to detect when the reaction is unaccompanied by some purely physical phenomenon such as emission of light, high temperature, etc. Nevertheless he does not think we are justified in discarding the idea that ionization may accompany all chemical action. Bloch[36] has repeated some of the earlier gas experiments of Reboul[37] and concludes that for the reaction $NH_3 + HCl$, ionization is doubtful; that none is produced by the reactions: $2NO_2 + O$; $SO_2 + O$ (contact method); $H_2 + S$; $S + O_2$; and decomposition of AsH_3. Only the case $2P + 5O$ gave ionization. Pinkus[38] employed an electroscopic method for two reactions: for $2NO + O_2$ he found no ionization; for the reaction $NO + Cl_2$ no ionization was found for

[34] F. Haber and G. Just, *Ann. d. Phys.* (4) 30, 411-15 (1909); *Zeit. Elektrochem.*, 16, 275-9 (1910); 17, 592 (1911); 20, 483-5 (1914); *Ann. d. Phys.* (4) 36, 308-40 (1911).

[35] G. Reboul, *Le Radium*, 8, 376-81 (1911).

[36] L. Bloch, *Comp. rend.* 149, 278-9 (1909); *Ann. de phys. et chim.*, 22, 370-417; 441-495 (1911).

[37] G. Reboul, *Comp. rend.* 149, 110-3 (1909).

[38] A. Pinkus, *Journ. de Chim. Phys.* 16, 201-27 (1918).

equivalent quantities nor for small excesses of either gas, but for large excess of NO some ionization appeared to occur. Broglie and Brizard[39] concluded, after an exhaustive study of the evidence, that chemical action produces ionization only when accompanied by a physical reaction such as passage of a gas through liquid, breaking a crystalline surface, luminescence, etc. They state that there is no ionization in the case of reactions of the following classes: (1) Between gases in the cold; (2) double decomposition in liquids; (3) dry decomposition of amorphous substances at slightly elevated temperature; (4) rupture of an inactive surface by bubbling. While there is ionization in the following cases: (1) Gases prepared by wet way; (2) vigorous reactions by projection into water; (3) dry actions accompanied by the decrepitation of crystals; (4) 2Na + O (moist), feeble ionization; (5) reactions with incandescence, such as flames, or combustion of metals in O_2 or Cl_2; (6) reactions with luminescence, such as the oxidation of P and of quinine sulfate.

The case may be summed up by stating that we have no definite evidence as yet of the production of ionization or the setting free of electrical charges by any homogeneous gas reaction at ordinary temperature, but that in the case of heterogeneous reactions or gas reactions at higher temperature we have undoubted cases of the liberation of charges, which may, however, not be directly the result of the chemical action, but the secondary result of some accompanying physical occurrence.

The determination of ionization produced in gaseous explosions has been undertaken by Haselfoot and Kirkby[40] for electrolytic hydrogen and oxygen at 80 mm. pressure, and for ozoimide (HN_3) by Kirkby and Marsh.[41] In the former case the M/N ratio was about 10^7 and in the latter about 100 times smaller. The explosion method has the disadvantage that whatever charges are liberated by the reaction are produced suddenly in large quantity so that the attainment of saturation current might be very difficult. However, from the small N/M ratio found it may be fairly concluded that the total liberation of charge is small compared with the number of molecules reacting,

[39] M. Broglie and L. Brizard, *Le Radium* 7, 164-9 (1910).
[40] E. E. Haselfoot and P. J. Kirkby, *Phil. Mag.* (6) 8, 471-81 (1904).
[41] P. J. Kirkby and J. E. Marsh, *Proc. Roy. Soc.* 87A, 90-99 (1913).

because, if N were anything like the same order of magnitude as M, the fields used would have drawn a greater number of ions than was observed to the electrodes before recombination could have occurred.

Chapter 10.

Photochemical Equivalence Law.

54. Einstein's Application of the Quantum Theory to Photochemical Action.

The inclusion of this subject, which does not properly form a part of the present monograph, has a two-fold object: (1) to enable a comparison between certain points of similarity which this branch of photochemistry shares with the other radiochemical effects which have been discussed in the foregoing chapters; and (2) to present the experimental investigations which have been brought to bear upon a test of the photochemical equivalence law since the appearance of the standard works on photochemistry.

It has been recognized by physicists for some time that the idea of the continuity of light as expressed by Maxwell's theory suffices for the explanation of optical phenomena, but that certain other phenomena, such as ionization by light, photoluminescence, and "dark radiation," require the introduction of an atomistic conception of radiant energy. This step was taken by Planck in his quantum theory according to which energy is radiated or absorbed only in integral units equal to $h\nu$, in which h is the Planck's constant (6.547×10^{-27} erg. sec.) and ν is the frequency of vibration. Einstein[1] has proposed the application of Planck's quantum theory to photochemical phenomena in the following form: $N = Q/h\nu$, in which Q is the absorbed heat required for the production of the chemical action, N is the number of molecules dissociated by light of the frequency ν.

In attempting to apply Einstein's law to actual photochemical reactions it is necessary to keep in mind that it applies only to the *primary light reaction.* As will be seen later, secondary reaction may intervene in such a way that the total quantity

[1] A. Einstein, *Ann. d. Physik* (4) 37, 832-8; 38, 881-4; 888 (1912). Also *ibid.* (4) 17, 132-48 (1905).

of chemical action resulting from the primary action may be either equivalent to it, or greatly in excess or deficiency, depending upon circumstances. In general it is not possible to measure the quantity of primary reaction directly, but only through the production of some secondary reaction. In order, therefore, that the test of the equivalence required by Einstein's photochemical law shall have any significance it is necessary to be able to measure a secondary reaction which is really equivalent to the primary. From the terminology of photochemistry the term *acceptor* has been used to designate the substance acted on by the product of the primary light reaction. Evidently the first requisite in testing the photochemical equivalence law is an acceptor which will give a measurable secondary reaction that is equivalent to the primary. There is as yet no theory according to which the action of a given acceptor toward a given primary product can be predicted. It is necessary in each case to try by experiment. Early failures to find "suitable" acceptors for the reactions investigated have rather retarded progress, but as experience is accumulated a more rapid development of the subject may be expected in the future.

55. Experimental Tests of the Law of Photochemical Equivalence.

Warburg[2] was one of the first to undertake experiments in this direction and was followed by Bodenstein, Lewis, and yet more recently by Nernst, his co-workers, and others. The results of the earlier work were summarized in 1913 by Bodenstein.[3] The following Table XV gives a list of reactions according to Bodenstein which he terms "primary light reactions," in which the number of molecules (M) acted on in the primary action are either equal to $h\nu$ or exceed it by small multiples. They may be regarded as cases in which Einstein's law is at least approximately applicable.

At the time that Bodenstein made the classification presented in Table XV he was of the opinion that the primary light reactions are the result of direct action of the positively charged ions left after the removal of an electron from the molecule. As

[2] E. Warburg, Extended series of papers in the *Sitzb. Berlin Akad. Wiss.* See later refs.

[3] M. Bodenstein, *Zeit. phys. Chem.* 85, 333 (1913).

TABLE XV

Primary Light Reactions According to Bodenstein

Reaction	*Authority*	*Absorption*	*hv/M*
$2HI = H_2 + I_2$	B.[4]	weak weak	? .....
$3\,O_2 = 2\,O_3$	R.[5] W.[6]	strong	1 for $2\,O_3$ (measd.)
$2NH_3 = N_2 + 3H_2$	R.[7] W.[8]	strong	4 (measd.)
$2H_2O = 2H_2 + O_2$	Not yet measd. without photochemical recombination.		
Anthracene→ dianthracene	L. & W.[9]	medium	1 to 0.7 (calcd.) 3 (calcd. by B.)
Decomp. Levulose	B. & G.[10]	medium	1.4 (calcd.)
$C_6H_4NO_2CHO$→ $C_6H_4NOCOOH$	W. & K.[11]	medium strong	9 (calcd.)
$S\lambda = S\mu$	W.[12]	medium	4 to 5 (calcd.)
Quinine oxidation by chromic acid	L. & F.[13]	medium	1.5 (calcd.)
$2\,O_3 = 3\,O_2$ (by Cl_2)	W.[14]	medium	1.7 (calcd.) 0.8 (calcd. by B.)

already stated, on account of the experimental evidence to the contrary Bodenstein[15] was forced to abandon his theory and to adopt the idea of Stark[16] that the primary light effect consists in *loosening* the valence electrons in such a manner as to render the molecule chemically active. This change of theory in no way affects the applicability of Bodenstein's idea of primary light reactions, for which he prescribes the following characteristics: (1) Proportionality between the quantity of chemical

[4] M. Bodenstein, *Zeit. phys. Chem.* 22, 23 (1897) ; 61, 447 (1907).
[5] E. Regener, *Ann. d. Physik* (4) 20, 1033 (1906).
[6] E. Warburg, *Sitzb. Akad. Wiss.* Berlin, 1912, 216.
[7] E. Regener, *loc. cit.*
[8] E. Warburg, *Sitzb. Akad. Wiss.* Berlin, 1911, 746; 1912, 216.
[9] R. Luther and F. Weigert, *Zeit. phys. Chem.*, 51, 297; 53; 385 (1905).
[10] D. Berthelot and H. Gaudechon, *Comp. rend.* 156, 707 (1913).
[11] F. Weigert and L. Kummerer, Ber. 46, 1207 (1913).
[12] A. Wigand, *Zeit. phys. Chem.*, 77, 423 (1911).
[13] R. Luther and G. S. Forbes, *ibid.*, 41, 1 (1902)
[14] F. Weigert, *ibid.*, 80, 103; *Zeit. Elektrochem.*, 14, 591 (1908).
[15] M. Bodenstein, *Zeit. Elektrochem.*, 22, 53-61 (1916).
[16] J. Stark, "Atomdynamik," Leipzig, 1911, Vol. II, p. 207.

reaction and the absorbed energy—with a corresponding law for reaction velocity. (2) Absence of influence of foreign substances, and (3) absence of influence of temperature, insofar as they do not influence the absorption of light. (4) One molecule reacting for each quantum of energy absorbed or for a small number of the latter.

Under secondary light reactions Bodenstein classed those which show a great excess over or deficiency from the requirements of Einstein's theory, and originally assumed that the excess action is due to the multiplied effect of the free wandering electrons, as already explained in the previous chapter. Upon being forced to abandon this theory for the same reason as in the case of the primary reactions, Bodenstein makes the assumption that a molecule which has received light energy (in the form of loosened valence electrons) does not lose it on combining with another atom or molecule, but produces a compound which is capable of imparting this energy to certain other molecules with which it comes into contact. To take the case of the H_2—Cl_2 reaction, he assumes that Cl_2 is activated, combines with ordinary H_2 molecules to form activated HCl which can impart its activity to Cl_2 and to O_2 (to explain dissipation of activity by inhibitors), but not to neutral gases like N_2, nor to H_2. In the following section will be presented a theory by Nernst assuming atomization of Cl_2 as the primary action. Without any distinction at present as to which theory has greater probability, Bodenstein's classification of the secondary light reactions has the same experimental weight as it originally carried and is therefore given in the following Table XVI.

Luther and Goldberg[17] have shown that in all the photochlorinations investigated by them oxygen acts as an inhibitor, and Bodenstein makes the generalization that oxygen inhibits all the secondary photochemical reactions except those in which it takes part as an oxydizing agent. The data of Bodenstein and Dux[18] on the kinetics of the photochemical interaction of hydrogen and chlorine served as a basis for Bodenstein's general photochemical theory, which he then applied to other photochemical reactions with the following modifications, which have been

[17] R. Luther and E. Goldberg, *Zeit. phys. Chem.*, 56, 43 (1906).
[18] M. Bodenstein and W. Dux, *ibid.*, 85, 297-328 (1913).

transformed by the writer into terms corresponding to his later theory instead of the original electronic theory:

(1) It is not always the substance primarily acted on by light which becomes activated for the secondary reaction.

(2) The velocity of the secondary effective reaction is not always excessively large compared with the ineffective reversion of the primarily affected substance to its original form.

(3) The secondary reaction is not always so great that the primary one can be neglected in comparison, as in the case of hydrogen and chlorine.

(4) Oxygen inhibition can be absent in case oxygen is the substance activated in the secondary reaction.

(5) Other substances can act as inhibitors and either take the place of or act jointly with oxygen.

In Table XVI the reactions are divided by Bodenstein into three classes: I. Those in which oxygen acts as inhibitor. II. Those in which oxygen is one of the components of the reaction and does not inhibit. III. Those in which the primary reaction can not be neglected in comparison with the secondary reaction. I_0 refers to the light absorption by A, the substance primarily acted on. B is the substance activated in the secondary reaction. C is in some cases a third reacting substance. dx/dt indicates velocity of chemical reaction in the usual differential form.

Recently a more rigorous test of Einstein's photochemical equivalence law has been made by Nernst[38] and Frl. Pusch.[39] Nernst emphasizes the necessity of paying attention to the primary reaction and of choosing an acceptor which neither multiplies nor diminishes the products of the primary action, but directly transforms them into the equivalent quantity of finally measured product. Frl. Pusch found hydrogen to be a very unsuitable acceptor in its reaction with bromine, the amount of action falling far short of theory. In an experiment with solar radiation of ten hours' duration, the quantity of bromine combined was 0.02 g., where 2.3 grams were predicted by theory. In experiments with a "nitra" (nitrogen filled) lamp as source of light, it was found that heptane, hexane and toluene all combine with bromine at a rate greater than theory, but hexahydroben-

[38] W. Nernst, *Zeit. Elektrochem.*, 24, 335-6 (1918).
[39] Frl. L. Pusch, *ibid.*, 24, 336-9 (1918).

TABLE XVI

Secondary Light Reactions According to Bodenstein

I. Equation $\frac{dx}{dt} = k. \frac{I_0.(A).(B)}{(O_2)}$

Reaction	*Authority*	*A.*	*B.*	*C.*	*Equation Observed*	*M/hν*
$H_2 + Cl_2 = 2HCl$	B. & D.[19]	Cl_2	Cl_2	.....	$k.(Cl_2)^2/(O_2)$	10^6
$2O_3 = 3O_2$	R.,[20] vB.,[21] W.[22]	O_3	O_3	.....	$k.(O_3)^2/(O_2)$	10^2-10^3
Hydrolysis of acetone	H. & W.[23]	.....	.....	.....	....	200
Oxalic acid + Uranyl nitrate	B.[24]	UO_2 $C_2H_4O_4$	$C_2H_4O_4$	.....	$k(UO_2 + C_2H_4O_4).C_2H_4O_4$	500
Hydrolysis of H_2PtCl_6	B. & J.[25]	H_2PtCl_6	H_2PtCl_6	.....	$k.(H_2PtCl_6)^2$	1 or 2
$2H_2O_2 = 2H_2O + O_2$	T.,[26] H. & W.[27]	H_2O_2	H_2O_2	.....	$k.(H_2O_2)^2/O_2$	100
Quinine + O_2	W.[28]	Ch-I[29]	Ch-II[29]	.....	$k. \frac{(Ch)^2}{(O_2)}$	1/200
Bleaching of dyes	W.,[30] Wi.,[31] (K)[32]	Dye	Dye	.....	....	1/200 (1/500)
$4HI + O_2 = 2I_2 + 4H_2O$	P.[33]	I′	O_2	.....	$k.(I').(O_2)$	10^6
$CHI_3 + O_2 = ...$	P.[34]	CH_3I	O_2	.....	$k.(CHI_3).(O_2\ ?)$	1 to 15

III. Equation dx/dt

$CO + Cl_2 = COCl_2$	Wn.,[35] C. & G.[36]	Cl_2	Cl_2	CO	$dx/dt = m + n/(O_2)$ for $Cl_2 + CO$ const. $dx/dt = k.(CO).(Cl)^{1-2}$	100
$Br_2 + C_7H_8 = HBr + C_7H_7Br$	B. & C.[37]	Br_2	Br_2	C_7H_8	$k.(Br_2).(C_7H_8)$	10^6

[19] M. Bodenstein and W. Dux, *Zeit. phys. Chem.*, 85, 297-328 (1913).
[20] E. Regener, *Ann. d. Physik* (4) 20, 1033 (1906).
[21] Frl. E. v. Bahr, *ibid.* (4) 33, 598 (1910).
[22] F. Weigert, *Zeit. phys. Chem.*, 80, 78 (1912).
[23] V. Henri and R. Wurmser, *Comp. rend.* 156, 1012 (1913).
[24] M. Boll, *ibid.*, 156, 1891 (1913).
[25] M. Boll and P. Job, *ibid.*, 154, 881 (1912) 155, 826 (1912); 156, 138, 691 (1913).
[26] A. Tian, *ibid.*, 151, 1040 (1910); 156, 1879 (1913).
[27] V. Henri and R. Wurmser, *loc. cit.*
[28] F. Weigert, *Nernst Festschrift*, p. 464.
[29] Ch-I is undissociated quinine sulfate; Ch-II is quinine ion or the free base.
[30] F. Weigert, *loc. cit.* (9).
[31] C. Winther, *Zeit. wiss. Phot.* 11, 92 (1911).
[32] W. Kistiakowski, *Zeit. phys. Chem.*, 35, 431 (1900).
[33] J. Plotnikow, *ibid.*, 58, 214 (1907).
[34] J. Plotnikow, *ibid.*, 75, 337; 385 (1910).
[35] M. Wildermann, *ibid.*, 42, 257 (1903); *Phil. Trans. Roy. Soc. Lond.* 199A, 337 (1902).
[36] D. L. Chapman and F. H. Gee, *Journ. Chem. Soc. Lond.*, 99_{II}, 1726 (1911).
[37] L. Bruner and S. Czernecki, *Bull. Acad. Cracovie A.*, 1910, p. 576.

zene appeared to be a suitable acceptor, and the following results were obtained by Frl. Pusch for several different exposures.

TABLE XVII

Test of Photochemical Equivalence Law, According to Frl. Pusch

Reaction: Bromine + Hexahydrobenzene.

Hours	*Milligrams of Bromine Combined*	
	(Found)	*Calcd. (Einstein's Law)*
8.25	2.08	1.82
22.33	5.95	5.38
20.25	5.72	5.10
24.25	5.66	5.70
24.00	5.82	5.51

Since the appearance of Bodenstein's classification, Warburg has tested the applicability of Einstein's law for a number of additional reactions. For the decomposition of ozone[40] he finds that, in dilute mixtures where the total pressure is one atmosphere, the secondary reaction furnishes a new confirmation of the law. Photolysis in aqueous solution was examined in the case of decomposition of nitrates to nitrites[41] using three wave lengths separately of the zinc arc: $\lambda = 0.214$, 0.257, and 0.274μ, respectively. The reaction was faster in slightly alkaline than in acid solution, was independent of the cation and of the degree of electrolytic dissociation. Einstein's law was not followed, the reaction being greater for short than for long wave lengths. The effect of the solute was suggested as the probable cause. The conversion of isomers was examined for the reactions: maleic → fumaric acid and the reverse action.[42] The chemical action found was about 4–13% of theory. The rate for maleic → fumaric increased with increase of λ but in a much greater ratio. The rate of the reverse reaction showed the opposite effect, thus contraverting

[40] E. Warburg, *Ber. Berlin Akad. Wiss.*, 1913, 644-59.
[41] E. Warburg, *ibid.*, 1918, 1228-46.
[42] E. Warburg, *ibid.*, 1919, 960-74.

the Einstein law. The effect of concentration was not great. Further tests in the case of ammonia decomposition[43] showed that either the law does not apply or that much ammonia is reformed. The application of the law was also not successful for the photolysis of HBr.[44]

56. Comparison of Photochemical Equivalence Law and Ionic-Chemical Equivalence.

Reference to Tables VII, XV and XVI will show that we have the same kinds of variation between theory and experiment both in photochemical and in α ray reactions. In both we have a number of experimentally investigated reactions in which agreement with theory is as good as could be expected in the present status of experimentation. We also have in both cases large departures from theory in either direction. On account of these points of similarity the question naturally presents itself as to whether the mechanism of reaction is not identical for the two different forms of radiation.

The most striking case of greatly excessive action among those hitherto investigated by α radiation has been shown to be that of hydrogen and chlorine where reaction exceeds theory by something like 10^4. Among the photochemical reactions we find the same reaction exceeding theory by 10^6. Bodenstein (*loc. cit.*) has expressed the view that the same mechanism must control both reactions. It would be of great interest to measure the increasing activity of hydrogen-chlorine mixtures with different forms of radiation to see whether the reactivity increases in the same proportion for all.

To explain the mechanism by which such large excess over theory can be attained, we have first the free electron theory of Bodenstein, which had to be abandoned as an explanation of photochemical effects, on account of the experimental demonstration of the absence of free electrons; but which may still hold for the α ray reactions, unless it be admitted with Bodenstein, that by analogy the same mechanism must hold for both. Second, we have the theory of loosened electrons of Stark for which Bodenstein has made the assumption that the light energy is retained after reaction and is imparted to other molecules, ren-

[43] E. Warburg, *Ber. Berlin Akad. Wiss.*, 1914, 872-85.
[44] E. Warburg, *ibid.*, 1916, 314-29.

dering them active. While there may be some question as to the probability of this theory, it has the advantage of very general applicability. In the following section it will be seen that Nernst has proposed an atomistic theory to account for the hydrogen-chlorine reaction, which is based on purely thermodynamic considerations. While it has great probability for that specific reaction it appears to be inapplicable directly to the other cases of excessive reaction. W. C. M. Lewis has proposed a radiation theory which is discussed in § 58.

The cases in which large deficiencies from theory are observed have all been explained up to the present by immediate reversal of the primary reaction. In this sense, an acceptor is a substance which combines with the products of the primary reaction without allowing them to recombine among themselves. On the other hand, the additional condition must be imposed upon a "suitable" acceptor, from the standpoint of photochemical equivalence, that it shall not by any other process multiply the output of the primary reaction.

57. Mechanism Proposed by Nernst for the Hydrogen-Chlorine Photo-Reaction.

Nernst has recently applied his heat theorem[45] to calculate the following heats of reaction:

$$Cl + Cl = Cl_2 + 106{,}000 \text{ cal.}$$
$$H + H = H_2 + 100{,}000 \text{ cal.}$$
$$Cl + H_2 = HCl + H + 25{,}000 \text{ cal.}$$
$$H + Cl_2 = HCl + Cl + 19{,}000 \text{ cal.}$$
$$\text{and } H + Cl = HCl + 125{,}000 \text{ cal.}$$

From the known absorption of chlorine for light of different wave lengths it can be calculated by the quantum theory within what spectral region chlorine can be dissociated into atoms. The calculation shows that this can be accomplished by the wave lengths known to produce chemical combination of hydrogen and chlorine and the assumption of the existence of free Cl atoms for the propagation of the photo-reaction is therefore justified. The heat of reaction shows that the combination of a Cl atom with a H_2 molecule and the subsequent splitting of

[45] W. Nernst, *Sitzb. Berlin Akad. Wiss.*, 1911, 65-90; also "Gruudlagen d. neuen Wärmesatzes" (1918), p. 133.

this unstable product to HCl and a free H atom take place with a large heat evolution, and therefore in the direction of spontaneous reaction according to the chemical free energy. Moreover, when a free H atom (just produced by the foregoing reaction) unites with a Cl_2 molecule we again have a reaction of the same nature. The Cl atom liberated by the latter reaction brings us back to the original system, and a cycle has been completed which may repeat itself indefinitely, except for the cross reaction of H and Cl atoms, and for the inhibitive effect of oxygen, which is assumed to remove the free Cl atoms from the field of action. By this purely thermodynamic method Nernst explains the multiplied secondary reaction in a mixture of H_2 and Cl_2, which accounts for the large departure from Einstein's law through the action of *free atoms*. In further support of the theory, Nernst calculates that a similar continuous cycle in the case of hydrogen and bromine is impossible, because one of the steps, $Br + H_2$, would not proceed spontaneously on account of a negative heat of reaction, —15,000 cals. And of course it is well known that a mixture of $H_2 + Br_2$ is not light sensitive at ordinary temperature. The further application of this or similar mechanisms to explain other cases of excessive action has not been attempted, but it is not without interest to note that in the only other two cases where the M/N value is as high as 10^6 (Table XVI), we have halide and hydrogen present in the system.

58. General Radiation Theory of Chemical Action.

In an extended series of investigations, Lewis and his co-workers[46] have proposed a radiation theory of chemical action which appears to be of fundamental importance in chemical kinetics, and which also has afforded additional confirmation of the applicability of Einstein's law. A general review of Lewis's theory and his deductions from it is pertinent to the subject of the present chapter.

It has long been recognized that the usual positive temperature coefficient of chemical reaction, which is of the order of a

[46] A. Lamble and W. C. McC. Lewis, *Journ. Chem. Soc. Lond.*, 105_{II}, 2330-42 (1914); 107_{I}, 233-48 (1915). R. H. Callow and Lewis, *ibid.*, 109_{I}, 55-67 (1916). R. O. Griffith and Lewis, *ibid.*, 109_{I}, 67-83 (1916). Lewis, *ibid.*, 109_{II}, 796-815 (1916). R. O. Griffith, A. Lamble and Lewis, *ibid.*, 111_{I}, 389-95 (1917). Lewis, *ibid.*, 11_{I}, 457-69; 111_{II}, 1086-1102 (1917); 113, 471-92 (1918); 115, 182-93 (1919); Rep. Brit. Assoc. (1915), p. 394.

2 to 3 fold increase for an interval of 10° C., can not be explained by the mere increase of kinetic energy of the reacting molecules. It has also been rather generally assumed that the molecules, before they react, must in some way be *activated,* and that this process is the one influenced by increase of temperature.

In 1889 Arrhenius[47] deduced a relation based on the assumption of a mass action equilibrium between active and inactive molecules, of the form: $d \log k/d T = A/T^2$, in which k is the velocity constant of chemical action, T is the absolute temperature, and A is one half of the energy required to change 1 Mol of inactive to active modification. This formula has since been shown to be of very general experimental applicability, although its theoretical basis is no longer tenable for the following reasons. The conception of Arrhenius, or indeed any other theory that attempts to explain velocity of reaction as controlled by temperature, leads directly to the consideration of the effect of catalysts, and that of Arrhenius to the prediction that the temperature coefficient should be diminished in a homogeneous system by the increase of the concentration of the catalyst. This prediction has not been confirmed by later work, including that of Lewis, who found that the temperature coefficient of the rate of hydrolysis of methyl acetate is independent of the concentration of acid. Recent work of Taylor[48] in the laboratory of Arrhenius has cast further doubt upon the existence of "active" molecules (in the sense of Arrhenius).

In 1914 Marcelin[49] treated the effect of temperature on velocity of reaction as a purely physical one dependent on the increase of the internal energy of the reacting molecule, and arrived at a formulation similar to that of Arrhenius: $d \log k/dT = E/RT^2$, in which E is defined as the critical energy that must be absorbed by the molecule to render it active. Lewis suggests that E be called the *critical increment* to emphasize that it is the *excess* energy that must be absorbed by the activated molecules above the average energy possessed by all molecules.

Rice[50] has developed in more exact mathematical form the same equation: $d \log k/dT = (V_c - V_m + 1/2(RT))/RT^2$, in

[47] Sv. Arrhenius, *Zeit. phys. Chem.*, 4, 226-48 (1889).
[48] H. S. Taylor, *Medd. Vetenskapsakad. Nobelinst.* 2, No. 34 (1912).
[49] R. Marcelin, *Comp. rend.* 158, 161 (1914).
[50] J. Rice, *Rep. Brit. Assoc.* (1915), p. 397.

which V_m is the mean value of the potential energy of the molecules and V_0 is the critical value which must be attained before chemical reaction ensues. Rice's formulation was used by Lewis in the development of the radiation theory applied to catalysis and later to chemical action in general. The application to catalysis has been adopted and explained by Rideal and Taylor.[51]

Lewis (*loc. cit.*) advances the hypothesis that the energy increment is imparted to the molecule by means of infra-red radiation, and that the Einstein Law is applicable to the energy absorption. The energy increment can be calculated directly from the temperature coefficient, as follows: $\log k_{35}/k_{25} = E/R(1/298 - 1/308)$. For the hydrolysis of methyl acetate the coefficient for a 10° interval at ordinary temperature is about 2.5, from which E is calculated to be 16,800 cals. per g.mol., or 1.03×10^{-12} ergs per single molecule. From Einstein's law Lewis calculates that for the infra-red radiation of $\lambda = 7.5\mu$ for methyl acetate (Coblentz [52]), $h\nu$ should be 0.262×10^{-12} ergs, or that $4h\nu$ should suffice to furnish the required energy E. Conversely Lewis has calculated from the velocity of the *H* ion (electrolytic) and its probable free path that it would have a vibration frequency falling in the region of the known absorption.

Lewis's suggestion that catalysis is in general a radiation phenomenon is supported by the theory of Trautz [53] and later by that of Krüger,[54] who showed that the processes of solution, solution pressure, solubility and electrolytic dissociation can be explained on the basis of radiation, which in turn can be related to the dielectric constant of the solvent. According to Lewis's conception the function of a catalyst is to absorb the infra-red radiation of the chemical system and to transfer the energy to the reacting molecule. In this sense catalysis is evidently but a special case of chemical reaction, where the absorption is accomplished by the catalyst instead of by the reacting substance itself. All reactions taking place in a solvent must be regarded as catalytic.

A still further step has been taken by Lewis (*loc. cit.*) in

[51] E. Rideal and H. S. Taylor, "Catalysis in Theory and Practice" (1919), p. 58 *et seq.*

[52] W. W. Coblentz, Pub. Carnegie Inst., Washington, 1905, 35.

[53] M. Trautz, *Zeit. wiss. Phot.*, 4, 160 (1906).

[54] H. Krüger, *Zeit. Elektrochem.*, 17, 453 (1911).

applying his theory to uncatalyzed homogeneous gas reactions. Strictly, Einstein's law is applicable only when n (index of refraction) $= 1$, which is true only in the case of gases. Lewis's theory applies to bimolecular homogeneous reactions of the type $2HI = H_2 + I_2$, with a fairly good agreement with the Einstein law. Heterogeneous (contact) catalysis can also be explained by Lewis's theory on the basis of Langmuir's [55] hypothesis regarding the spacial distribution of molecules and atoms at the interface between two phases. The energy increment is lowered at the contact surface, which is in agreement with the lower temperature coefficients of heterogeneous chemical reactions.

Lewis [56] has recently pointed out the anomalous case of *monomolecular* homogeneous gas reactions, which differ from the bimolecular reactions in the pronounced failure of Einstein's law. The value of the velocity constant for the rate of dissociation of PH_3 observed by Trautz and Bhandarkar [57] is about 10^7 greater than calculated by Lewis from Einstein's law on the assumption of continuous absorption. For discontinuous absorption the discrepancy becomes still greater. In view of the approximate agreement for bimolecular reactions this great departure for monomolecular reactions is all the more notable.

Baly [58] has applied the quantum theory to spectroscopic and fluorescent phenomena. According to his theory a molecule may absorb radiation by quanta of a given frequency and radiate a larger number of quanta as a result of chemical action at a lower frequency. Chemical action, excessive from the standpoint of Einstein's law, can then be explained by re-absorption of this internal radiation, a process that will result in further chemical action that may be multiplied to very large quantities from one quantum primarily absorbed. Baly proposes this explanation for the large excess observed in the thermal decomposition of phosphine and also for the photochemical decomposition of hydrogen peroxide and hydrolysis of acetone.[59]

It should be mentioned that Perrin [60] independently arrived

[55] I. Langmuir, *Journ. Amer. Chem. Soc.* 38, 2221 (1916).
[56] W. C. McC. Lewis, *Phil. Mag.* (6) 39, 26-31 (1920).
[57] M. Trautz and D. S. Bhandarkar, *Zeit. anorg. Chem.* 106, 95 (1919)
[58] E. C. C. Baly, *Phil. Mag.* (6) 40, 1-15; 15-31 (1920).
[59] V. Henri and R. Wurmser, *Comp. rend.* 156, 1012 (1913).
[60] J. Perrin, *Ann. de Physique* (9) 11, 5-108 (1919).

at a general radiation theory of chemical action which is very similar to that of Lewis.

The type of radiation that is involved in Lewis's theory is very different from the corpuscular forms that are treated in this monograph and also from those of the usual photochemical effects. In the infra-red absorption the energy increment is not a large fraction of the chemical energy of the reaction, whereas, in the case of the corpuscular and photochemical radiation effects, the energy applied is usually largely in excess of the net chemical energy involved in the reaction.

With reference to the emission of infra-red radiation by chemical reactions, the recent work of David [61] should be cited, who has shown that the explosive combination of oxygen with coal gas and with hydrogen results in the emission of radiation of wave lengths $\lambda = 2.8\mu$ and 4.4μ. Although the temperature of reaction in the experiments of David is estimated at 1200°, he is of the opinion that the radiation is due to the chemical action and not to temperature effect.

Further contributions to the radiation theory of chemical action have been very recently made by Langmuir,[62] Rideal,[63] Lindemann [64] and Tolman.[65] Langmuir makes a fundamental inquiry into the basis of the radiation hypothesis of chemical action and concludes (1) that it has not been satisfactorily demonstrated that the radiation emitted by a chemical action, as calculated from the temperature coefficient, falls in the absorption region of the system; (2) that the total radiation is not nearly sufficient to account for chemical activation and that the radiation hypothesis is untenable. Langmuir believes that the internal energy of the molecule is the ultimate source of its activation. Lindeman points out (as does Langmuir also) that according to the radiation hypothesis many reactions should be photo-sensitive which fail to exhibit this effect. Tolman adopts the view of Lewis, Perrin and Marcelin that the similar form of the Arrhenius equation and the Wien radiation law justifies the radiation hypothesis of chemical action. Tolman employs

[61] W. T. David, *Phil. Mag.* (6) 39, 66-83; 84-95 (1920). *Trans. Roy. Soc. Lond.*, 211, 375; *Proc.*, 85, 537 (1911).

[62] I. Langmuir, *J. Am. Chem. Soc.*, 42, 2190-2205 (1920).

[63] Eric K. Rideal, *Phil. Mag.* (6) 40, 461-6 (1920).

[64] F. A. Lindemann, *ibid.* (6) 40, 671-4 (1920).

[65] R. C. Tolman, *J. Am. Chem. Soc.*, 42, 2506-28 (1920).

the principles of statistical mechanics to develop the Rice-Marcelin equation and also makes many other applications important to chemical kinetics. Rideal employs a formula of Langmuir and Dushman to develop the equation for velocity of reaction: $\frac{dn}{dt} = \nu . e^{\frac{-h\nu}{kt}}$, in which n is the number of molecules reacting per second, ν is the frequency, and all other symbols having the usual meaning. Applying this to the decomposition of PH_3, the velocity constant is calculated to be 3.5×10^{-3}, the same order of magnitude as that observed 10.2×10^{-3}.

Daniels and Johnston[66] have recently investigated the thermal and photochemical decomposition of gaseous N_2O_5. The thermal action is monomolecular and proceeds at room temperature. The critical increment as calculated from the temperature of the velocity of decomposition is independent of the temperature. Its value, 24,700 calories, indicates according to the radiation theory that the reaction should be catalyzed by light of wave length = 1.16μ. Photochemical investigation failed to confirm this prediction. Light in the region 400—460μμ does accelerate the decomposition, but only in the presence of NO_2. The interesting theory is proposed that the catalytic effect of NO_2 is due to its absorption of blue light over a wide spectral range and that through fluorescence, radiation is emitted in the infra-red region where its absorption lines coincide with those of N_2O_5, causing decomposition of the latter. Experimental evidence of the actual fluorescence of the NO_2 and of the decomposition of N_2O_5 by radiation in the infra-red region remains to be obtained.

[66] F. Daniels and E. H. Johnston, *J. Am. Chem. Soc.*, 43, 53-81 (1921).

Chapter 11.

Positive Rays and Recoil Atoms.

59. General Nature of Positive Rays.

In 1886 it was observed by Goldstein[1] that if he used a perforated cathode in examining electrical discharge through air at low pressure, luminous beams of rays could be seen traversing the space back of the cathode, *i. e.* on the side away from the anode, which apparently came through the channels in the cathode. On account of their mode of formation or demonstration Goldstein called them "canal" rays. It has since been shown that they are the positively charged gaseous ions which, at low gas pressure, attain sufficient velocity toward the cathode or negative pole to carry them through the perforations into the space behind, where they can be observed by means of phosphorescent screens or by their action on the photographic plate.

In 1898 Wien[2] demonstrated the deflection of the canal rays by a strong magnetic field. Since this time J. J. Thomson[3] has conducted a series of investigations which have resulted in discoveries of the greatest importance both to physics and chemistry. It has been recommended by Thomson[4] that the more correctly descriptive term, *positive rays of electricity,* be used instead of canal rays.

Thomson[4] has elaborated a technique to determine by means of deflection in a combined magnetic and electrostatic field the e/m value of each type of positive ray. The effects due to the superposition of the electric and magnetic fields simultaneously applied have been analyzed by Thomson in the following way: If the forces are applied parallel to the axis of *z*, the y and z deflections of the particle are given by the two equations:

[1] E. Goldstein, *Sitzb. Akad. Wiss.*, Berlin, 1886, p. 691; *Wied. Ann.*, 64, 38 (1898).
[2] W. Wien, *Verh. deut. phys. Ges.*, 17, .. (1898).
[3] J. J. Thomson, *Phil. Mag.* (6) 21, 225-49 (1911); 24, 209-53 (1912).
[4] J. J. Thomson, "Rays of Positive Electricity" (1913).

$y = e/mv.A$ and $z = e/mv^2.B$, in which A and B depend only on the strengths of the magnetic and electrical fields, respectively, and the distance of the projection from the point of deflection, and can be made constant for a given experiment. In the absence of any field all positive rays would pass through the narrow aperture in the cathode and be recorded on the photographic plate at the same spot $x = l$, the distance of the plate from the source. Under the selective action of the two forces the particles are sorted out and no two strike the plate at the same spot unless they are moving with the same velocity and have the same e/m value. By combining the two equations just given above we have: $v = y/z.B/A$ and $e/m = y^2/z.B/A^2$. The first shows that y/z is constant for all particles moving with a given velocity v, no matter what their charge or mass is, and, therefore, will all lie on the plate in a straight line passing through the undeflected position of the particles. The second equation shows that for the same kind of particles, y^2/z is constant no matter what their velocity; hence, all particles of the same kind will trace on the plate a parabola with its vertex at the undeflected position of the particles. Each parabola will represent a different kind of particle. This principle has been used by Thomson and his co-workers as a method of positive ray analysis, which will be described in the following section.

60. Thomson's Method of Positive Ray Analysis.

Thomson's experimental method has been very fully described in his "Rays of Positive Electricity." The latest modification of the apparatus, termed mass-spectrograph, has recently been thoroughly described by Aston.[5] Only a few of the most important experimental features will be mentioned here before passing on to a consideration of the results. A very large spherical bulb (20 cms. diameter) is employed for the discharge between the anode and cathode in order to favor the passage of current at very low pressure. A silica anticathode is used which has the advantages of infusibility and of giving no disturbing X radiation. The two cathode slits which give direction to the beam of positive rays are of aluminium 2 mm. long and 0.05 mm. wide. The space between the slits 10 cms. long is kept at the

[5] F. W. Aston, *Phil. Mag.* (6) 39, 611-26 (1920).

highest possible vacuum by a side tube of charcoal immersed in liquid air. Beyond the slit system is the electrical field, 200 to 500 volts, between two flat brass surfaces 2.8 mms. apart and 5 cms. long. Beyond the electrical field is the magnetic field in which the rays pass between the pole pieces of a large DuBois magnet of 2500 turns, the faces of which are circular, 8 cms. in diameter and 3 mms. apart. The current for the magnet is provided by a set of large accumulators. A current of 0.2 ampere just brings the H lines onto the plate, while 5 amperes just bring the singly charged Hg lines into view. The camera chamber is provided with a special plate holder arranged so that the plate can be shifted for several different exposures without opening the chamber. Exposures from 20 seconds for the H lines, up to 30 minutes or more are required. The discharge in the large chamber is maintained by means of a large induction coil with a Hg coal-gas break. 100 to 150 watts are passed through the primary circuit, and the bulb itself takes 0.5 to 1.0 milliampere at 20,000 to 50,000 volts.

The measurement of the photographic plates to determine the mass of the positive rays is made by means of a special comparator capable of measuring in two directions. Theoretically an unknown mass may be determined from *one* known on the same plate, but practically, greater accuracy is obtained by bracketing the unknown with several known lines just as in ordinary spectral line measurements.

The photographic method does not yield an insight into the relative quantities of the different rays. This has been accomplished by Thomson by substituting for the camera a Wilson tilting electroscope to determine the total charge under the following conditions. The condenser into which the positive rays are received is provided with a parabolic slit, which in principle might be moved to any part of the field to admit rays of a given mass for quantitative measurement by means of their charge. Instead of actually moving the slit it is made stationary and the rays of different masses are successively brought to it by varying the magnetic field strength.

Thomson has determined the various types of ions which are produced in different gases. The variety of ions for a given substance is very large compared with electrolytic ions. Certain characteristics have been pointed out by Thomson which are

very useful in determining what mass is represented by a given m/e value. *Multiple charge is found only in the case of atoms.*[6] Molecules either of elements or of compounds have not been found to be multiply charged with either sign.[6] The heavy atoms show multiple charge to a higher degree than do the lower ones. There is no apparent relation between the chemical properties of the element, such as valence and the number of charges. Mercury can have as many as eight charges, oxygen, nitrogen, and neon two; hydrogen never more than one, which is the only element examined for which no multiple charges have ever been found.

61. Isotopes of Neon.

As early as 1912 Thomson obtained some evidence by the positive ray method of the existence of particles of mass 22 in neon gas. Aston[7] has recently determined the mass spectra of neon by the positive ray method with an accuracy of 1 in 1000 parts. The measurements show conclusively that neon consists *of two* isotopes of masses 20 and 22, in the proportion of about nine of the former to one of the latter, which accounts for the observed atomic weight 20.2. There is also a faint indication of a third isotype of mass 21 in a proportion estimated as less than *1%. If this third isotope* proves to have real existence it will constitute a very interesting continuation of the system of triads like iron, nickel and cobalt, which was predicted in 1895 by Reynolds,[8] purely from analogy with the three other well known groups of triads.

Attempts have been made by Lindemann and Aston[9] to separate the two modifications of neon by fractional distillation and by fractional diffusion through pipe-clay. Later Lindemann[10] discussed the theory of the separation and decided that the negative result obtained was the one to have been expected under the experimental conditions, in the case of fractional distillation. The fractional diffusion resulted in an apparent difference of density of about 0.7%, while an automatic method

[6] Except in case of fluorides of boron and silicon. (F. W. Aston, *Phil. Mag.* (6) 40, 630 (1920).

[7] F. W. Aston, *Phil. Mag.* (6) 39, 449-55 (1920).

[8] E. Reynolds, *Nature*, March 21, 1895.

[9] F. A. Lindemann and F. W. Aston, *Phil. Mag.* (6) 37, 523-35 (1919).

[10] *F. A. Lindemann, ibid., 38, 173-81 (1919).*

started in 1914 gave a difference of only 0.3%. It can therefore be said at the present time that the diffusion method in the case of neon has given positive results but the differences are too small to be conclusive.

62. Discovery of Other New Isotopes by Aston.

Still more recently Aston[11] has extended the search for isotopes by the positive ray method to other elements. His investigations have yielded results which, while absolutely astounding to chemists in one sense, must be regarded as having been foreshadowed by Prout's[12] hypothesis more than one hundred years ago. At the time of writing (Oct., 1920) eighteen elements have been examined by Aston with the following results, H, He, C, N, O, F, P, and As give a pure mass spectrum indicating but one isotope, as would be expected from their whole number atomic weights. The results for the other elements can be seen in the following Table XVIII. The case of bromine is of particular interest. Although its atomic weight (79.92) is quite close to 80, there appears to be no isotope of the mass 80 at all, but two isotopes in almost equal quantities of 79 and 81.

As the atomic weights of the elements increase it becomes more difficult to get a definite resolution of isotopes of masses differing by one or two units, since the percentage difference is small. The whole number rule on the basis of O = 16 has not hitherto been departed from in any case except hydrogen. This may be related to the absence of electrons in the hydrogen nucleus. At any rate it seems very well established that the departures of the ordinary atomic weights from unity is to be accounted for by a mixture of whole number isotopes. The occurrence of isotopes appears to become more common among the elements of higher atomic weight; apparently, there are more complex than simple elements. The influence this is likely to have in practical and theoretical chemistry has been expressed by Aston (*loc. cit.*) as follows. "The very large number of different molecules possible when mixed elements unite to form compounds would appear to make their theoretical chemistry

[11] F. W. Aston, *Nature*, 105; p. 8; p. 546; pp. 617-19 (1920). *Phil. Mag.* (6) 39, 611-25; 40, 628-34 (1920).

[12] W. Ostwald, *Grundriss d. allgemeinen Chemie* (1899), p. 41. S. L. Bigelow, "Theoretical and Physical Chemistry" (1912), p. 87.

TABLE XVIII

Isotopes[13] *of the Ordinary Elements According to Positive Ray Analysis by Aston*[14]

Element	*Atomic Number*	*Atomic Weight*	*Minimum No. of isotopes*	*Mass in the Order of Intensity*
H	1	1.008	1	1.008
He	2	3.99	1	4
B	5	10.9	2	11, 10
C	6	12.00	1	12
N	7	14.01	1	14
O	8	16.00	1	16
F	9	19.00	1	19
Ne	10	20.2	2	20, 22, (21)
Si	14	28.3	2	28, 29, (30)
P	15	31.04	1	31
S	16	32.06	1	32
Cl	17	35.46	2	35, 37, (39)
A	18	39.88	(2)	40, (36)
As	33	74.96	1	75
Br	35	79.92	2	79, 81
Kr	36	82.92	6	84, 86, 82, 83, 80, 78
X	54	130.2	5	(128, 131, 130, 133, 135)
Hg	80	200.6	(6)	(197-200), 202, 204

almost hopelessly complicated, but if, as seems likely, the separation of isotopes on any reasonable scale is to all intents impossible, their practical chemistry will not be affected, while the whole number rule introduces a very desirable simplification into the theoretical aspects of mass."

The attempts of Lindemann and Aston to separate the two modifications of neon have already been referred to. A number of experiments to this end have already been carried out with other elements, and doubtless in the future we may expect much activity in the same direction. It also appears highly desirable that a series of very accurate atomic weight determinations should be made of the complex elements from different sources to

[13] A list of the radioactive isotopes will be found in Appendix, Table B.
[14] F. W. Aston, *Phil. Mag.* (6) 40, 633 (1920).

ascertain if the isotopes always occur mixed in the same proportion.

No attempt to separate isotopes has as yet been conclusively successful. In the case of radioactive and ordinary lead, Richards and Hall[15] obtained wholly negative results by the use of fractional crystallization. Harkins[16] and his co-workers have been engaged in the attempt to separate chlorine by diffusion and have obtained encouraging though not finally positive results. The theoretical aspects of the separation of chlorine by various methods have been the subject of much recent discussion.[17]

Brönsted and v. Hevesy[18] report the separation of mercury into two fractions by distillation, one having a density 0.999980, the other of 1.000031, compared with that of the original as unity.

63. General Properties of Recoil Atoms.

The treatment of the chemical action produced by recoil atoms does not fall under the title either of α particles or electrons, but since the emission of α radiation and, to a much smaller degree, of β radiation is always accompanied by recoil, and since it has recently been shown that the recoil atoms are capable of producing chemical action, it appears appropriate to treat the subject briefly in the present monograph. Before proceeding to the chemical effects it will be necessary to consider the more general characteristics of recoil atoms.

When a radioactive atom emits an α particle in a given direction the parent atom, or atomic residue, receives an impulse in the opposite direction, which has very aptly been termed *recoil.* The atom receiving the recoil is termed the recoil atom. Recoil atoms were first studied by Miss Brooks,[19] by Hahn,[20] and by Russ and Makower[21] as a means of separating the recoiling radioactive substance in a pure state.

[15] T. W. Richards and N. F. Hall, *Journ. Amer. Chem. Soc.* 39, 531-41 (1917).

[16] W. D. Harkins, *Science*, 51, 289 (1920).

[17] T. R. Merton and H. Hartley, *Nature*, 105, 104 (1920); W. D. Harkins, *ibid.*, 105, 230; D. L. Chapman, *ibid.*, 105, 487; 642; F. Soddy, *ibid.*, 105, 516; A. F. Core, *ibid.*, 105, 582.

[18] J. N. Brönsted and G. v. Hevesy, *Nature*, 106, 144 (1920).

[19] Miss H. T. Brooks, *Nature*, July 21, 1904.

[20] O. Hahn, *Verh. deut. phys. Ges.*, 11, 55 (1909).

[21] S. Russ and W. Makower, *Proc. Roy. Soc.* 82A, 205 (1909).

Rutherford[22] has shown that when a particle of mass m is ejected with velocity v from an atom of mass M, the residual atom of mass M–m recoils with a velocity V, according to the relation (M–m)V = mv. In the case of Ra A of atomic weight 218 (Table I) the expulsion of the α particle of mass 4 at a velocity of 1.82×10^9 cms. sec.$^{-1}$ results in a recoil atom of Ra B with a velocity of 3.4×10^7 cms. sec.$^{-1}$. This velocity is sufficient to ionize a gas in which the recoil radiation takes place, as has been shown by Wertenstein.[23] The velocity and kinetic energy of the recoil atoms may be calculated to be about 1/50 to 1/60 that of the corresponding α particles. The fraction in each case is equal to $\frac{m}{M-m}$.[24]

Wertenstein,[25] in the laboratory of Mme. Curie, has made the most exhaustive investigation of recoil atoms yet undertaken. He has called the recoil atoms from Ra A *a* particles. They have a range in air at atmospheric pressure of 0.14 mm., and in hydrogen of 0.83 mm. This range in air is about 1/350 that of the α particle; and since the kinetic energy of the *a* particle is 1/50 that of the α particle, it is evident that the expenditure of energy by the *a* particle is about seven times as great per length of path as that of the α particle. This does not mean that the ionization is seven times as great, because the proportion of energy expended in producing ionization is somewhat smaller in the case of *a* particles, but Wertenstein found that the ionization produced by α particles becomes *in maximo* about five times as great as that of α particles over the same path.

This knowledge of recoil atoms will suffice at least for a preliminary survey of what may be expected if they produce chemical action in anything like the same proportion to their ionizing powers that α particles do. The two most prominent properties to be kept in mind are their very limited range and their great intensity of action within that range. In a vessel of infinitely large volume in which the *a* particles would expend all their energy in the gas system without striking the wall, the comparative effect of the recoil atoms would be less than 2%, or very

[22] E. E. Rutherford, "Radioactive Substances and Their Radiations" (1913), p. 174.

[23] L. Wertenstein, *Comp. rend.* 152, 1657 (1911).

[24] Meyer and v. Schweidler, "Radioaktivität" (1916), p. 129.

[25] L. Wertenstein, *Thesis*, Paris, 1913.

small. On reducing the volume or pressure, the effect of the easily absorbed recoil atoms remains constant, while the α particles expend part of their energy in the wall, which part was shown in Chapter VI to be ineffective in producing chemical action. As the volume is further diminished the α particles have still shorter paths and the effect of the recoil atoms becomes relatively greater and greater. In very small volumes and at low pressures it is evident that the ionizing and chemical effects of the recoil atoms would exceed the effect of α particles by several fold. That this is exactly the case found experimentally with respect to chemical action will be shown in the following section.

64. Chemical Reaction Produced by Recoil Atoms.

In § 43 the influence of the size of the reaction vessel on the rate and extent of the combination of hydrogen and oxygen in equivalent proportions mixed with radium emanation was demonstrated. The general law found experimentally and based in principle upon the average path of α particles in the reaction vessel is for spheres: $\log P/P_0 \big/ E_0(e^{-\lambda t} - 1) = 84.1/D^2$, in which P_0 is the initial pressure of electrolytic gas in mm. of Hg, P the pressure of the same at any time t, E_0 is the initial quantity of radium emanation in curies, $e^{-\lambda t}$ expresses the rate of decay of emanation, and D is the diameter of the spherical reaction vessel in cms. The expression was shown to be true for spheres with diameters up to about 10 cms. containing electrolytic mixture not exceeding one atmosphere pressure. On attempting to apply the kinetic equation represented by the left hand side of the equation just given, to the case of a sphere of diameter as small as 1 cm., it was found that a velocity constant could not be obtained as in the case of larger spheres (Table XI). The experimental data of Lind[26] are shown in Table XIX for a sphere of about 1 cm. diameter which should have, according to the general relation for larger spheres, a value of velocity constant ($k\mu/\lambda$) of 90.4, but, as will be seen, the value of the first measurement was 104.6, which rose as the reaction progressed to a value of 220.5. If the velocity constant be calculated for each separate interval, as explained in § 45, the rise of the $(k\mu/\lambda)'$ becomes still more marked, as may be seen in the table. But the time intervals

[26] S. C. Lind, *Journ. Amer. Chem. Soc.* 41, 533 (1919).

are still too large. To avoid this, Curve 1 in Fig. 7 was plotted with pressure as ordinates and time as abscissæ. The interpolated values of P in Table XIX were then taken from the curve from which the values of $(k\mu/\lambda)'$ in the last column were calculated. Curve 1a in Fig. 7 shows the course of the normal pressure reduction by α rays alone in larger vessels, as calculated from the general equation.

TABLE XIX

Effect of Recoil Atoms in Producing an Abnormal Rate of Combination of Hydrogen and Oxygen in a Small Sphere

Vol. = 0.470 c. c. Diam. = 0.9647 cm. E_0 = 0.04234 curie.
Normal $k\mu/\lambda$ = 90.4.

Actual Data			*Calculated from Actual Data*		*Interpolated Data*			
Days	*Hrs.*	*P. in mm. Hg*	$k\mu/\lambda$	$(k\mu/\lambda)'$	*Days*	*Hrs.*	*P.*	$(k\mu/\lambda)'$
0	0.0	507.8	.....	.....	0	0.0	507.8	.....
					0	6.0	425.0	95.6
0	15.67	310.3	104.6	104.6	0	12.0	354.0	102.7
					0	18.0	290.0	117.1
0	19.90	271.2	105.9	111.2	1	0.0	233.0	134.4
					1	6.0	187.0	141.6
0	23.67	235.1	111.4	142.9	1	12.0	150.7	145.0
					1	18.0	123.0	148.8
1	15.33	135.4	121.4	139.0	2	0.0	96.0	182.4
					2	6.0	73.0	210.9
1	19.00	119.0	123.4	148.7	2	12.0	51.5	278.9
					2	18.0	33.0	377.6
2	5.00	76.7	134.8	195.0	3	0.0	19.5	461.7
					3	3.0	14.0	594.3
3	0.33	18.8	181.3	349.6	3	6.0	9.9	646.0
					3	9.0	7.5	528.5
3	15.42	5.0	220.5	483.3	3	12.0	5.7	535.1
					3	15.42	5.0	228.3

To ascertain whether the abnormality observed for the 1 cm. sphere could be accounted for by the action of recoil atoms added to that of α particles, the following analysis of the results was

made. If 90.4 is the normal velocity constant for α particles, 180.8 will represent a velocity where the action of recoil atoms is just equal to that of α particles under the same conditions. By plotting the $(k\mu/\lambda)'$ values from the last column of Table XIX as Curve 2 of Fig. 7, it was found that $(k\mu/\lambda)'$ becomes equal to 180.8 at a gas pressure of 118 mms. At any other pressure the proportion of chemical action being produced by each type of radiation can be estimated on the following basis:

1. That the chemical effect of the recoil atoms remains constant down to a very low pressure at which they also begin to reach the wall in large proportion without being stopped by the gas.

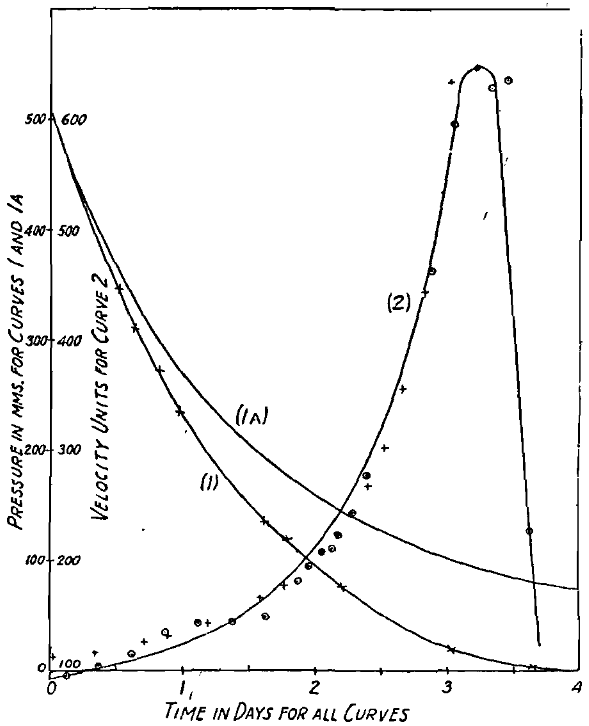

Fig. 7.

2. That the chemical effect of the α particles will at all pressures be proportional to the pressure.

For example, at 118 mms. the two effects are equal to each other and one can arbitrarily place each equal to 118. At any other pressure, 50 mms. for example, the recoil atom effect, which

for convenience will be called the R effect, would still have the value 118; the α effect now will have the value 50; the combined effect is 168; the *abnormality factor,* or the ratio of the observed abnormal effect to the normal α effect, will be $(R + \alpha)/\alpha = 168/50 = 3.36$. Table XX shows this same analysis carried to its upper and lower limits.

Comparison of the last two columns of Table XX shows that the general trend of the experimental and calculated values of the velocity constant $(k\mu/\lambda)'$ is the same. The calculated values will be found plotted in Curve 2 of Fig. 7 as +, the interpolated values taken from Table XIX as ⊙. The agreement between theory and experiment is satisfactory. The maximum value found, 632, when divided by the normal α value 90.4, shows that the maximum ratio $(R + \alpha)/\alpha$ is 6.99. According to Wertenstein (*loc., cit.*) the maximum ionization due to recoil atoms from Ra A is five times that of the α particles over the same path, which would be a combined ionization *six* times that of the α particles alone. Remembering that Wertenstein's statement refers to recoil atoms from Ra A alone, while with emanation we are dealing with three different sets of α particles, the agreement is perhaps as good as could be expected. At least one must be convinced that recoil atoms cause the combination of hydrogen and oxygen at ordinary temperature, and approximately in the same proportion to their ionizing powers as in the case of α particles.

At first thought it must appear surprising that the chemical effect of recoil atoms can be observed at fairly large pressures. One must consider, however, that the radius of the reaction bulb is only 4.8 mms., and that the average path within the spherical bulb is only about 6/10 of this, or about 2.9 mms.; moreover, the range of the *a* particle in the electrolytic mixture will be about 0.3 mm. at standard pressure (calculated from Wertenstein's measurements for air and for hydrogen), and would be still greater for recoil atoms of Ra C. These facts, considered together with the intensity of the energy expense by recoil atoms, make it evident that the pressure and bulb dimensions at which the chemical effect of recoil atoms manifests itself are quite concordant with Wertenstein's ionization data.

Finally it should be inquired whether the chemical effect of recoil atoms will not also be observed in larger spheres at low

pressure. The answer must be affirmative, with certain reservations. By referring to Table XI it will be seen that for the 2-centimeter sphere there is an unmistakable tendency for $k\mu/\lambda$ to increase slightly toward the end of the reaction, which tendency would be brought out much more distinctly by calculating for $(k\mu/\lambda)'$. However, the quantity of gas to be acted on in larger spheres, beginning with normal pressure, is so much greater than in a 1-cm. one, that before low pressures are attained, the emanation is nearly exhausted and the effect on the $k\mu/\lambda$ value is largely masked.

TABLE XX

Analysis of the Recoil Atom Effect (R) and the α Ray Effect (α) in Causing Electrolytic Hydrogen and Oxygen to Combine in a 1 cm. Sphere

R effect = constant = 118. α effect proportional to pressure = P.

$\alpha = P$ (mm. Hg)	$R + \alpha$	$(R + \alpha)/\alpha$	$(k\mu/\lambda)'$ Calcd.	$(k\mu/\lambda)'$ Found (Curve 2)
10	128	(12.80)	...	...
20	138	6.90	622	632
30	148	4.93	444	446
40	158	3.95	356	376
50	168	3.36	303	350
60	178	2.97	268	292
70	188	2.69	242	267
80	198	2.48	223	240
90	208	2.31	208	223
100	218	2.18	195	204
110	228	2.07	186	192
120	238	1.98	177	182
130	248	1.91	172	166
140	258	1.84	166	162
150	268	1.79	161	153
200	318	1.59	143	133
250	368	1.47	132	118
300	418	1.39	125	112
400	518	1.29	116	100
500	618	1.24	113	95
600	718	1.19	107	...

The almost vertical drop in Curve 2, Fig. 7, after passing the maximum is due to practical exhaustion of the electrolytic gas mixture. The experimental method employed was the same as that described in § 42, and is not applicable to extremely low pressures with accuracy. It would be very interesting to examine this reaction, using a refined pressure method in order to investigate more precisely the course of the reaction near its end. Theoretically the abnormality factor should continue to rise until the gas is completely exhausted.

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TABLE XX

Analysis of the Recoil Atom Effect (R) and the α Ray Effect (α) in Causing Electrolytic Hydrogen and Oxygen to Combine in a 1 cm. Sphere

R effect = constant = 118. α effect proportional to pressure = P.

$\alpha = P$ (mm. Hg)	$R + \alpha$	$(R + \alpha)/\alpha$	$(k\mu/\lambda)'$ Calcd.	$(k\mu/\lambda)'$ Found (Curve 2)
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Chapter 12.

Atomic Disintegration by α Particles.

65. Scattering and Impacts of α Particles.

The great potency of the α particle as an agent in the production of chemical action has been frequently emphasized in preceding chapters. The reactions treated up to the present have been of ordinary molecular character. Very recently Rutherford has demonstrated conclusively for the first time that under certain conditions the α particle is capable of producing a much more fundamental chemical change, namely, the disintegration of the atom into new kinds of atoms. Although such changes are spontaneously taking place among the radioactive elements, Rutherford has presented the first evidence that can be accepted without doubt, of the artificial disintegration of the atom. These intra-atomic reactions fall very properly within the confines of radiochemistry. It will therefore be attempted to give a brief non-mathematical description of Rutherford's work which led up to and proved absolutely this discovery of preeminent importance.

The investigations of Rutherford and his co-workers in Manchester and more recently in Cambridge of the phenomena accompanying the passage of α particles through matter have been remarkably successful in furnishing insight into the question of atomic structure. As has been pointed out, the flight of the α particle of high velocity carries it in a straight line through a large number of molecules or atoms, which are ionized by the removal of a single electron from each molecule encountered. The α particle suffers no deflection in the ordinary encounter, but has its velocity gradually diminished until it is no longer able to produce ionization. Toward the end of its path, when its velocity is much reduced, the α particle is more subject to deflection or scattering, and occasionally it experiences a very large deflection or is actually turned backward in its path. The

great rarity of the occurrence of the large deflections led, as has already been pointed out, to the Rutherford-Bohr atomic model according to which most of the atomic mass is centered in an extremely minute nucleus with a positive charge equal to the atomic number of the atom, which for the heavier elements is somewhat less than half the atomic weight.

The large deflections or reversals of the α particle are then attributed to a close impact of the particle with the nucleus of the atom encountered. These impacts were first investigated using thin sheets of the heavier metals. The law governing the deflection or scattering was worked out by Geiger and Marsden,[1] on the basis of repulsion inversely with the square of the distance from point charges. The experimental scattering was in good agreement with this theory and it was calculated that the direct impact represents an approach of the α particle to the nucleus within about 3×10^{-12} cm. *in the case of heavy atoms.*

The case for light atoms is different in two important respects. First, on account of the smaller nuclear charge the repulsion of the positively charged α particle is much less than in the case of heavy atoms, and the α particle is therefore able to approach much closer to the nucleus, approximately ten times as close. This close approach on impact produces radical differences in the result of the repulsion which will be described later. Second, on account of the smaller mass of the nucleus of light atoms they are repelled to greater distances than the heavy ones. Under favorable circumstances the light atoms are projected forward at a velocity which carries them beyond the range of the impelling α particle and can be detected and counted by the scintillation method. This opens new possibilities for their investigation, which have been utilized by Rutherford as will be recounted in the following paragraphs.

Darwin[2] has shown that the law of scattering and repulsion predicts that all the light atoms up to and including oxygen should be capable of being repelled by a doubly charged α particle to a distance exceeding the range of the α particle in the same medium, provided that the atom repelled has a *single* positive charge. Evidently, if the repelled atom has a double charge, no atom heavier than helium could be repelled beyond

[1] H. Geiger and E. Marsden, *Phil. Mag.* (6) 25, 604 (1913).
[2] C. G. Darwin, *Phil. Mag.* (6) 27, 499 (1914).

the range of the α particle, without borrowing energy from some other source. It was to test this prediction that Rutherford undertook the experiments which have led to other highly significant conclusions.

66. Swift Hydrogen Atoms.

In the case of the repulsion of a hydrogen atom as the result of an intimate impact with an α particle, we have a case of great simplicity in some respects. On account of its having but a single electron it is impossible for the nucleus of the hydrogen atom to carry more than a single positive charge. On account of its elemental nature there is little probability of the hydrogen atom being changed or disrupted by impact with an α particle. On the theory of impact one should expect a hydrogen atom to be set into swift motion as the result of a direct nuclear encounter with an α particle, with a velocity 1.6 times that of the α particle. The range to be expected for the swift hydrogen atom would be about four times that of the α particle, and its kinetic energy 0.64 of the energy of the α particle. Marsden [3] found that the passage of α particles through hydrogen did produce a large number of faint scintillations on a zinc sulfide screen which could be detected far beyond the range of the α particle. Rutherford [4] has made a very detailed study of the subject which confirmed the theoretical predictions. The swift H atoms have a range in hydrogen of 100 cms., about four times that of the α particle in the same gas. The number projected straight forward by an α particle of range 7 cms. is 30 times greater than required by the simple theory of scattering. The probable explanation is the distortion of the nucleus by such close approach, which was about 3×10^{-13} cm., or approximately the same as the diameter of an electron. The direction of the swift H atoms is mainly the same as that of the α particle, and the velocity of different particles is uniform. On reducing the velocity of the α particle the direction of the H atoms becomes more varied, approaching the requirements of the law of scattering as to distribution, but still exceeding theory in number. In traversing one cm. of hydrogen about 10^5 α particles produce one swift H atom, which means

[3] E. Marsden, *Phil. Mag.* (6) 27, 824 (1914). E. Marsden and W. C. Lantsberry, *ibid.*, 30, 240 (1915).

[4] E. E. Rutherford, *Phil. Mag.* (6) 37, 537-61; 562-71 (1919).

that out of 10^9 hydrogen atoms ionized, only 1 is set into swift motion as the result of a direct nuclear impact.

Since the nuclear impact is an atomic phenomenon, the long range swift atoms can be produced by radiating either the element or any compound of it. This fact has proved a source of some embarrassment in the case of hydrogen, since it is very difficult to remove water vapor and possibly other compounds containing hydrogen from the field of action. As a consequence every source of α radiation has been found to give some swift H atoms continuously. So persistent is this phenomenon that it has suggested the possibility of the emission of H particles from the nucleus of the radioactive element itself in the same way that α particles are emitted. Later evidence obtained by Rutherford (*loc. cit.*) does not appear to support such an hypothesis strongly, but the question is still regarded by Rutherford as a subject requiring further investigation.

Both magnetic and electrostatic methods of deflection have been used by Rutherford in examining the charge and velocity of the swift H atoms. The charge was shown to be unipolar positive, and the maximum velocity is 1.6 times that of the α particle, as required by theory.

67. Experiments of Rutherford with Other Light Atoms.

After obtaining such important results with hydrogen Rutherford[5] proceeded to investigate the propulsion of some of the other light *atoms* to distances beyond the range of the α particle. Assuming *singly* charged particles as the result of impact, it was predicted from Darwin's formulation that the swift nitrogen atom ought to have a range 1.33 times that of the α particle producing it, and that oxygen should similarly have the value 1.12. Both of these gases were examined by Rutherford, who found numerous scintillations beyond the α range in the region 7–9 cms. from the source, which in number corresponded closely to that found in the hydrogen experiments, indicating that the nature of the impact was similar. The range found for nitrogen was approximately that predicted by theory. In the case of oxygen the range was not very different from that found for nitrogen. This value greater than theory was rather puzzling,

[5] E. E. Rutherford, *Phil. Mag.* (6) 37, 571-87 (1919).

but Rutherford was inclined to believe that the swift particles were in both cases the singly charged oxygen or nitrogen atoms.

The improbability of this assumption was pointed out by Fulcher,[6] who showed that the propulsion of a singly positively charged atom of nitrogen (or oxygen) involves the assumption that the other orbital electrons are carried with the swift atom. According to Fulcher's contention the forces binding these remote electrons to the nucleus are not sufficient to overcome their initial inertia at the moment of impact, when they would have to take on a speed of 10^9 cm. sec.$^{-1}$ in less than 10^{-18} sec. According to Fulcher the remaining electrons would either be left behind initially or soon be brushed off by contact with other molecules of the gas traversed. The swift particles could not be nitrogen or oxygen atoms without electrons, for such multiply charged atoms would have shorter ranges than were observed. Fulcher suggests that the swift particles are α rays produced by the disruption of nitrogen by the impact. Of course doubly charged helium atoms could not be projected beyond the range of the bombarding α particle unless they got additional energy from some other source. Fulcher suggested that the impact results in the explosion of the nitrogen atom so that the internal atomic energy becomes available, just as in the case of the radioactive changes. This would represent a type of "artificial radioactivity" which will be discussed in § 69. The only difficulty of Fulcher's assumption lay in its failing to explain the uniform direction of the swift particles in the direction of the α particle. The result of an atomic explosion would be expected to cause the ejection of α particles in any direction according to the law of chance. The probability of atomic disruption by α particles had already been established for nitrogen in another way by Rutherford, which will be considered in the following section.

68. Decomposition of Nitrogen and Oxygen.

In June 1919 Rutherford[7] reported the observation of an anomalous effect in nitrogen bombarded by α rays. A closed metal box containing an intense source of Ra C at 3 cms. from the end was provided with an opening in the end covered with a silver plate of stopping power equivalent to 6 cms. of air. The

[6] G. S. Fulcher, *Science* 50, 582-4 (1919).
[7] E. E. Rutherford, *Phil. Mag.* (6) 37, 581-7.

ZnS screen was placed just outside the opening at 1 mm. distance. The number of "natural" scintillations on this screen, owing to some unavoidable source of swift H atoms, is increased by exhausting the box. On admitting dry air or CO_2, the number of scintillations is diminished in the ratio to be expected from the increase of stopping power of the gas column. But if *nitrogen* is admitted the number of scintillations *increases*. Nitrogen from different sources was tried and various attempts were unsuccessful in explaining the phenomenon without assuming that H atoms were being bombarded from nitrogen atoms by α rays. The observed range of the swift particles was too great for them to have a mass greater than that of the H atom; the effect seemed to depend on the presence of nitrogen and to be proportional to its concentration, so that no other conclusion was left open except that nitrogen is disrupted by α ray bombardment and that one of the products of the disruption is the swift H atom.

Upon going to Cambridge, Rutherford[8] continued his work on the nuclear constitution of atoms, and devised a comparison method of examining the magnetic deflection of the swift particles in order to estimate the mass. The results of the experiments confirm that the long range particles from nitrogen are particles with the same mass as the H atom, as Rutherford had previously supposed. The investigation of the shorter range particles from oxygen and nitrogen has in part confirmed the predictions of Fulcher. In both cases they appear to be doubly charged helium atoms and not the singly charged atom of nitrogen or oxygen; but instead of having the usual mass 4 of the He atom, a mass of *3* was found which according to Rutherford represents an isotope of helium. In the case of oxygen no very long range particles corresponding to those of hydrogen and nitrogen are found, and Rutherford suggests that the oxygen nucleus is composed of four helium atoms of mass 3 and one of mass 4 and two nuclear or binding electrons giving a net positive charge of 8. In the case of nitrogen we have two different modes of disruption, one giving swift doubly charged atoms of helium of mass 3, the other giving swift H atoms of mass 1. Since the number of the former exceeds the latter by five to ten fold, Rutherford assumes that the two modes of disruption are independent of each other and do not occur simultaneously from the same atom. The nuclear

[8] E. E. Rutherford, Bakerian Lecture, *Proc. Roy. Soc.* 97A, 374-400 (1920).

structure of nitrogen proposed by Rutherford is four doubly charged helium atoms of mass 3 and two singly charged H atoms of mass 1 and three binding electrons giving a net positive charge of 7. If the H atoms have an interior position in the nucleus with reference to the He atoms, as Rutherford suggests, this might account for the greater frequency of the disruption accompanied by expulsion of a swift He atom.

69. Artificial Radioactivity.

The experimental results of Rutherford just discussed in § 68 appear to confirm Fulcher's prediction (§ 67) that the shorter range swift particles from nitrogen (and also those from oxygen) are not the singly charged N and O atoms, but are doubly charged He atoms (of mass 3). Rutherford estimates that the gain in energy of motion resulting from the impact must be at least 8%, even though the subsequent motion of the disintegrated nucleus and of the bombarding α particle be neglected. Evidently this additional energy is derived from the internal atomic energy of the disrupted atom, and we have direct proof of Fulcher's "artificial radioactivity." If the excess energy utilized by the swift particle is in reality not more than 8% of the energy of the bombarding α particle, Fulcher's difficulty of explaining the uniform direction of the swift particles can perhaps be dismissed. There is no evidence that the atomic nucleus is entirely disrupted, and Rutherford inclines to the view that only a single particle is ejected from each atom and discusses the possible isotopic modifications of atoms of lower atomic weight which remain as the result of the loss of a single atom in the two types of disruption. As yet there is experimental evidence only of the swift particles of range longer than the α particle and we have no direct evidence as to the nature of the residue.

Rutherford points out that the amount of disintegration is exceedingly small. If in the case of nitrogen only one α particle in 300,000 succeeds in getting near enough to the nucleus to liberate a swift H atom with sufficient velocity for it to be detected, the entire α radiation from a gram of radium, if wholly absorbed in nitrogen, would generate only about 5×10^{-4} mm.^{3} of hydrogen per year. It is quite possible however that much disintegration takes place through the liberation of particles of

slower velocity which can not be detected. It is also possible that *high velocity electrons* possess sufficient energy to bring about such a disintegration, because their close approach to the nucleus would be accompanied by an attraction instead of a repulsion. In this case we should expect to find the effect possibly more pronounced in the case of the atoms of high atomic number than of lower. It is possible that some of the inert gases found by various authorities by spectral methods may have resulted from intense electronic bombardment of the electrodes. The results of further experiments in this direction may be awaited with a great deal of interest. Rutherford does not consider it impossible that penetrating X rays may have sufficient energy to cause atomic disintegration.

It may not be without interest to observe that the discovery of radioactivity came about as the result of the search for the spontaneous emission of X rays. We now have the situation reversed; having discovered radioactivity and the spontaneous disintegration of the atom, we turn back to its artificial disruption, and enter upon an era of renewed activity in the quest of "transmutation."

APPENDIX

Table A. Decay of Radium Examination According to L. Kolowrat

Time: Days	Time: Hrs.	Quantity Remaining $e^{-\lambda t}$	Δ 0.00	Time: Days	Time: Hrs.	Quantity Remaining $e^{-\lambda t}$	Δ 0.00	Time: Days	Time: Hrs.	Quantity Remaining $e^{-\lambda t}$	Δ 0.00
	0	1.00000	375	1	11	0.76913	575	4	3	0.47592	353
	0.5	0.99625	372	1	12	0.76338	570	4	6	0.46533	345
	1	0.99253	742	1	13	0.75768	567	4	9	0.45498	337
	2	0.98511	736	1	14	0.75201	562	4	12	0.44486	330
	3	0.97775	730	1	15	0.74639	557	4	15	0.43496	323
	4	0.97045	726	1	16	0.74082	554	4	18	0.42528	315
	5	0.96319	719	1	17	0.73528	549	4	21	0.41582	308
	6	0.95600	715	1	18	0.72979	545	5	0	0.40657	3004
	7	0.94885	709	1	19	0.72434	542	5	4	0.39455	2915
	8	0.94176	703	1	20	0.71892	537	5	8	0.38289	2829
	9	0.93473	699	1	21	0.71355	533	5	12	0.37158	2745
	10	0.92774	693	1	22	0.70822	529	5	16	0.36059	2664
	11	0.92081	688	1	23	0.70293	525	5	20	0.34994	2585
	12	0.91393	683	2	0	0.69768	522	6	0	0.33960	2509
	13	0.90710	678	2	1	0.69246	517	6	4	0.32956	2435
	14	0.90032	672	2	2	0.68729	514	6	8	0.31982	2363
	15	0.89360	668	2	3	0.68215	509	6	12	0.31037	2293
	16	0.88692	663	2	4	0.67706	504	6	16	0.30019	2225
	17	0.88029	657	2	6	0.66698	496	6	20	0.29229	2160
	18	0.87372	653	2	8	0.65705	489	7	0	0.28365	2096
	19	0.86719	648	2	10	0.64726	482	7	4	0.27527	2034
	20	0.86071	643	2	12	0.63763	475	7	8	0.26714	1974
	21	0.85428	639	2	14	0.62813	468	7	12	0.25924	1915
	22	0.84789	633	2	16	0.61878	461	7	16	0.25158	1859
	23	0.84156	629	2	18	0.60957	454	7	20	0.24414	1804
1	0	0.83527	624	2	20	0.60050	447	8	0	0.23693	1751
1	1	0.82903	620	2	22	0.59156	440	8	4	0.22993	1690
1	2	0.82283	614	3	0	0.58275	432	8	8	0.22313	1649
1	3	0.81669	611	3	3	0.56978	422	8	12	0.21654	1600
1	4	0.81058	605	3	6	0.55711	413	8	16	0.21014	1553
1	5	0.80453	601	3	9	0.54471	404	8	20	0.20393	1507
1	6	0.79852	597	3	12	0.53259	395	9	0	0.19790	1462
1	7	0.79255	592	3	15	0.52074	386	9	4	0.19205	1419
1	8	0.78663	588	3	18	0.50916	378	9	8	0.18637	1377
1	9	0.78075	583	3	21	0.49783	369	9	12	0.18087	1326
1	10	0.77492	579	4	0	0.48675	361	9	18	0.17291	1268

APPENDIX—(*Continued*)

Table A. Decay of Radium Examination According to L. Kolowrat

Time		*Quantity Remaining* $e^{-\lambda t}$	Δ *0.00*	*Time*		*Quantity Remaining* $e^{-\lambda t}$	Δ *0.00*	*Time*		*Quantity Remaining* $e^{-\lambda t}$	Δ *0.00*
Days	*Hrs.*			*Days*	*Hrs.*			*Days*	*Hrs.*		
10	0	0.16530	1212	14	16	0.07136	0519	21	12	0.02086	01496
10	6	0.15803	1159	15	0	0.06721	0489	22	0	0.01906	01367
10	12	0.15107	1108	15	8	0.06329	0461	22	12	0.01742	01250
10	18	0.14442	1059	15	16	0.05961	0434	23	0	0.01592	01142
11	0	0.13807	1013	16	0	0.05613	0409	23	12	0.01455	01044
11	6	0.13199	0968	16	8	0.05287	0385	24	0	0.01330	00954
11	12	0.12619	0925	16	16	0.04979	0362	24	12	0.01216	00872
11	18	0.12063	0885	17	0	0.04689	0341	25	0	0.01111	00797
12	0	0.11533	0846	17	8	0.04416	0321	25	12	0.01015	00728
12	6	0.11025	0809	17	16	0.04159	0303	26	0	0.00928	00637
12	12	0.10540	0773	18	0	0.03916	02809	27	0	0.00775	00532
12	18	0.10076	0739	18	12	0.03579	02567	28	0	0.00647	00444
13	0	0.09633	0701	19	0	0.03271	02346	29	0	0.00541	00371
13	8	0.09072	0660	19	12	0.02990	02144	30	0	0.00452	.....
13	16	0.08543	0622	20	0	0.02732	01960	40	0	0.000747	.....
14	0	0.08046	0586	20	12	0.02497	01791	50	0	0.000123	.....
14	8	0.07577	0552	21	0	0.02282	01637		∞	0.00000	

APPENDIX—TABLE B

List of Radioactive Isotopes[9] *by Groups*[10]

Atom. Wt.	o (VIII)	I a	I b	II a	II b	III a	III b	IV a	IV b	V a	V b	VI a	VI b	VII a	VII b	Atom. Wt.
197			**Au**													197
200					**Hg**				RaG							200
204							**Tl**		(AcD_2)**Pb**							204
206									$(\beta) ThD_2$		**Bi**					206
207							β AcD	{82}	β RaD		β RaE		α **RaF**			207
208						{81}	β ThD		β AcB	{83}	$\alpha \beta AcC_1$		αAcC_2			208
210							βRaC_2		β ThB		$\alpha \beta ThC_1$		αThC_2			210
(211)									β RaB		$\alpha \beta RaC_1$	{84}	α RaC′			(211)
212													α AcA			212
214													α ThA			214
(215)													α RaA			(215)
216														{85}		216
218																218
(219)	α AcEm															(219)
220	α ThEm {86}															220
222	α **RaEm**															222
(223)				α **AcX**												(223)
224		{87}		α ThX												224
226				α **Ra**	{88}											226
(227)																(227)
228				$(\beta) MsTh_1$		(β) Ac		α RdAc								228
230						$\beta MsTh_2$	{89}	α RdTh								230
232								α *Io*	{90}							232
234								α **Th**								234
238								βUX_1		βUX_2	{91}	αU_2	{92}			238
												α $\mathbf{U_1}$				

α and β indicate the type of radiation. The atomic number for each group is indicated in { }.

[9] A list of the isotopes of the ordinary elements, hitherto discovered, will be found in Table XVIII, § 62.

[10] K. Fajans, *Phys. Zeit. 16*, 464 (1915).

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